ABSTRACT

Multiscale Modeling of Thermoplastic Elastomers for Enhanced Mechanical Properties

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To relate the mechanical responses of hard-soft copolymer systems with their microstructures, a coarse-grained molecular dynamics (CGMD) approach is employed. With the generic bead-spring polymer model mapped from atomistic simulations, this dissertation first studies the morphology of structures with various hard-soft compositions and interactions between hard beads. Following that, this dissertation investigates the enhancement mechanism of hard domains under tensile and shear loading conditions with pressure. The energy factor that denotes the interaction between hard beads dominates the micro-phase separation and morphology. The numerical experiments also show that pressure is the most crucial factor in shear-under-pressure tests, with larger pressure leading to higher shear resistance of the copolymers.

To help understand thermoplastic polyurea and polyurethanes (TPUs) from a macro-mechanical perspective, mechanical properties of both hard and soft domains are calculated using the CGMD model. The viscoelastic behaviors of soft matrix and hard-soft copolymers are computed from the stress autocorrelation function (SACF). The stress relaxation indicates that the soft matrix is in a rubbery state at room temperature while hard domains are “solid-like” and can be viewed as elastic solids in a macroscale model. The dynamic shear modulus is then fitted with Prony series using a two-step optimization method. In addition, local elastic constants of hard domains are computed using the stress-strain fluctuation method with purely local stress and local strain. The results can be used as inputs for macroscale models for copolymers and can provide guidelines for
understanding and designing polymeric materials.

Once the macroscale mechanical properties of both phases are obtained from the CGMD model, continuum scale simulation of TPUs is needed to understand the reason for their excellent blast mitigation properties. To make clear how hard and soft domains interact with each other in a continuum scale, Finite Element Analysis (FEA) is used to study the linear viscoelastic response of polyurea by introducing a gradient interphase area around hard domains. Niblack-algorithm-based AFM image binarization is employed to provide geometry inputs while the viscoelastic master curves of soft matrix are obtained via Dynamic Mechanical Analysis (DMA) data at low frequencies and Molecular Dynamics (MD) estimations at high frequencies. Interphase property gradually changes when the distance from hard domains increases. Both spatial and property distributions of this interphase region affect the viscoelastic response of the copolymer system.

To quantitatively investigate how the structural and property features of the interphase affect the system’s energy storage and dissipation, we represent the interphase region with a 15-element vector. Statistical features of the vector represent physical meanings of the interphase. For example, length of nonzero elements means the interphase thickness. Borrowing the concepts of decision tree and random forest from machine learning, we apply a ranking algorithm to identify feature significance on four mechanical responses. Results show that modulus of hard domains determines the instantaneous storage modulus change while the volume fraction of hard domains dominates the long-term modulus change. Following volume fraction of hard domains, total interphase volume fraction and shifting factor distribution mainly affects $\tan \delta$ peak decreases while the mean and maximum value of shifting factors determines the $\tan \delta$ peak shifting.
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Chapter 1 Introduction

1.1 Background and Motivation

Thermoplastic polyurea and polyurethanes (TPUs) represent a subcategory of thermoplastic elastomers (TPEs) and are among the most promising commercialized segmented copolymers due to their versatile properties and the advantage of melt processability (thermoplastics). TPUs have attracted increasing attention in coating industry and structural systems subjected to impact loading because of their low wave speeds, acoustic impedances and good dissipative properties [1-3]. TPUs serve as coating materials on tunnels, bridges, roofs, parking decks, storage tanks, and more recently on buildings, vehicles and military armors to impart impact resistance to structures [3]. TPUs’ extensive benefits over existing epoxy adhesives and rubber linings in terms of impact, abrasion and corrosion resistance make structures more resistant to damages from a bomb blast and less likely to fragmentation, thus improve the survivability of structures [4, 5].

Among all kinds of TPUs, polyurea is the generic term for the block copolymer formed from reaction of di-isocyanates with polyamines [6, 7]. Introduced in 1989 by Texaco Chemical Company, polyurea was first advertised as a product in the coating industry [8], however, recent studies have shown promising mechanical responses of polyurea that are not only limited to the coating applications but venture into critical applications such as reinforcement of metal structures against blast and impact loads as in body armors and helmets [9-12]. This material with high potential for blast/ballistic-impact mitigation is now frequently used as gun-fire/ballistic resistant and explosion/blast mitigation coating or inter-layer in blast-resistant sandwich panels for military vehicles and structures, as well as in external and internal wall-sidings and foundation coating for
Excellent performances of TPUs originate from their typical structural features. Polyurea is an elastomeric copolymer formed by the rapid chemical reaction between an isocyanate and an amine (Figure 1). Due to the presence of strongly polar “urea linkages”, polyurea is typically phase segregated into hard segments which associate to form hard domains and a soft matrix [5, 13, 14]. Figure 2 shows a typical taping-mode AFM image of such a phase segregation [15]. The hard segments formed by hydrogen bonding of the urea-linkage tend to aggregate into larger domains (hard domains) and increase the overall polymer strength due to its high glass transition temperature \( T_g \). The soft segments consist of relatively flexible polyamine/polyol chains in which the hard domains are embedded and act as a flexible continuous matrix for the network of hard domains. Since the hydrogen bonding of the urea-linkages provides the linking between chains, polyureas and polyurethanes are often recognized as microphase-segregated and thermoplastically cross-linked elastomers. The \( T_g \) of the soft domains is around \(-60^\circ C\), while the \( T_g \) of the hard domain is above \(100^\circ C\) [16]. These two distinct \( T_g \)s make polyurea’s behavior qualitatively similar to elastomers reinforced by nanosized fillers. It has been recognized that the formation of the physical cross-links in block and segmented copolymers were driven by the micro-phase separation, which stemmed from the intrinsic incompatibility or thermodynamic immiscibility between the soft and hard segments and/or crystallinity of the hard-soft components [17]. Therefore, the microphase separation of hard and soft domains is responsible for the versatile properties of this broad class of polymer [2, 18].
Chemical structure of polyurea.

An example of a typical tapping-mode AFM image of a polyurea showing a rod-like morphology of the hard segments [15].

In light of the growing applications of TPU for improving impact resistance, a thorough understanding of their mechanical behavior under various loading conditions, together with solutions to problems like the effect of both hard and soft domains on mechanical responses and how the two domains interact with each other, become necessary in order to understand TPU’s behavior and optimize their performance during normal operation conditions as well as during impact events.

Substantial efforts have been made to characterize the structural and chemical details of TPU through various experimental techniques [1] and atomic scale simulations [13, 19]. With the aid of the MD methods, various properties of theoretical elastomers have been reported [20-22].
However, most of them were mainly concerned with the structures and morphologies of the hard-soft copolymers without much attention to the mechanical properties. The macroscopic mechanical properties of TPUs are dependent upon several microstructural factors, such as the composition, chemical nature of the units, and the morphology [23]. In addition to experimental investigations of their microstructures and morphologies, many efforts have also been made to understand the dynamic response of elastomers at strain rates of $10^3 \text{s}^{-1}$ using split-Hopkinson (or Kolsky) pressure bar apparatus [24-26]. Since high strain rates and high pressures often occur under impact and ballistic loading in defense applications, a series of plate impact experiments have been conducted to study the response in those extreme conditions using the pressure-shear plate impact (PSPI) technique [27-30]. It was found that the shearing resistance is highly dependent on the pressure applied prior to shear. Many molecular dynamics simulations have also been conducted at both the atomic [13, 19] and coarse-grained [20, 31, 32] levels. Through these simulations, shear resistance was verified to be strongly dependent on pressure, and it was suggested that the molecular weight of the soft segments can significantly influence the shearing resistance [14]. Similar investigations were carried out for diblock and multiblock copolymers, indicating that the multiblock architecture of polyurea might impart polyurea with smaller, more deformable, and interconnected hard domains that lead to improved energy dissipation and lower shock speeds [20]. However, the mechanisms controlling shear resistance in these systems are not well understood, including the role of the hard segments and how hard domains interact with the soft matrix.

While systematic numerical experiments using MD are needed to explore the enhancement mechanisms induced by hard segments and provide details of pressure effects and other factors on
shearing resistance, calculation of mechanical properties for each phase in hard-soft copolymers is also critical. Those experimentally inaccessible properties can serve as inputs for continuum-scale studies. Most importantly, relating those local properties to microstructural features is crucial to develop design guidelines for more efficient and durable materials. The aforementioned $T_g$ s of soft and hard domains indicate their states at room temperature and lead us to compute the viscoelastic behavior of the rubbery soft matrix and elastic constants of the hard domains.

1.2 Coarse-Grained Molecular Dynamics Model for Hard-Soft Copolymers

Although several experimental measurements have explored the enforcement of mechanical properties brought by the existence of hard domains, few quantitative descriptions are reported. One reason is that in order to understand the role of hard segments, it is essential to have the polymer samples with desired distribution and interactive force of hard segments, which is too expensive and practically impossible for experiments. Molecular dynamics (MD) simulation, on the other hand, provides an alternative way. It allows us to prepare virtual polymers and to perform numerical experiments. MD has been proven to be a powerful technique for exploring the microscopic nature of atomic motion and has shown broad applications in physics, chemistry, material science, and other areas.

Ideally, one would like to use atomistically detailed models because they can accurately capture the subtleties in the interactions between the polymers and are very helpful for understanding and predicting the atomistic-scale properties of polymers. It also has flexibility in potential choices: relatively simple potentials can work well for specific properties [33] while more complicated potentials that can handle chemical reactions [34] or are designed to very accurately reproduce
vibrational spectra [35] can also be found in the literature. However, because of the intrinsically slow dynamics, a direct prediction of the large-scale dynamics and rheology from such detailed models is computationally unattainable (except for the case of unentangled or slightly entangled polymers) [36]. For most TPUs we study, the hydrogen bonding of the urea-linkage provides inter-chain joining and they are highly entangled, therefore, the atomic scale polyurea model only represents a completely mixed state of the material and micro-phase separation process cannot be generally investigated. As a result, the unit cell can only provide information about the fully mixed material state/properties, the information about the material that resembles the soft-matrix phase of polyurea [13, 19]. In addition, atomistic details sometimes obscure the properties of interest in a larger scale. Therefore, new developments that enable an expansion of the time and length scales have been considered. For example, lattice based models have a long history in the simulation community because of their efficiency [37, 38], a polymer chain can be represented by simpler models such as united-atom model, the bead-spring model [39], the bond fluctuation model [40], and etc. All these models are considered to represent physical objects obtained by averaging the microscopic details of the atomistic models, being generally called the “coarse-grained model” [41].

Coarse grained polymer models neglect the chemical details of a specific polymer chain and only keep those degrees of freedom that are deemed important for the particular range of interest. They only include the excluded volume and topology (chain connectivity) as the properties determining the universal large-scale behavior of polymers. All coarse grained molecular dynamics (CGMD) models have the repeating unit or monomer to represent a section of typically
4-6 backbone atoms of a chemically realistic chain and MD techniques are employed to study their dynamics, whereas Monte Carlo techniques are used for the lattice models and for efficient equilibration of the continuum models [37, 38, 42]. Interactions are only defined between those super-atoms and a reduction in the number of pair interactions can be two orders of magnitude. In addition, the resulting coarse-grained potentials are much softer than atomistic potentials so larger time steps can be used. Typical increases in the time step are between 10 and 100. Thus in the worst case, the efficiency increases are 3 to 4 orders of magnitude [43].

CGMD models usually make use of atomic-level pair correlation functions, either from atomistic simulations or from experiments, as data to parameterize against. This strategy has the advantage that detailed structural information is incorporated into the CGMD model. Among various CGMD models, those of the bead-spring type suggested by Kremer and Grest [39] has been widely employed as a generic theoretical model in the realm of polymer physics [44, 45]. Recent simulations have also demonstrated its ability to capture many mechanical characteristics of polymers [21]. These models retain the form of the non-bonded interactions used in the chemically realistic modelling, i.e. use an interaction either of the Lennard-Jones or of the exponential-6 type. The repulsive parts of these potentials generate the necessary local excluded volume, whereas the attractive long-range parts can be used to model varying solvent quality for dilute or semi-dilute solutions and to generate a reasonable equation of state for polymeric melts.

1.3 Mechanical Property Calculation in CGMD Model for Hard-Soft Copolymers

1.3.1 Calculation of Viscoelastic Properties in MD Simulations

The linear viscoelastic spectrum is one of the primary fingerprints of polymer solutions and
melts, carrying information of relaxation processes in the system. While the dynamics and viscoelastic properties of polymer melts are now generally well understood from a theoretical viewpoint [46, 47], experimental measurements still suffer from a limited scope of timescale. Amirkhizi et al.[48, 49] used dynamic mechanical analysis (DMA) tests which cover most of the transition zone and developed master curves of storage and loss moduli using the principle of time–temperature superposition to access both very short and very long-time scales inaccessible experimentally. Nevertheless, the predicted loss moduli were significantly lower than those calculated from ultrasonic wave dissipation at high frequencies [48].

On the computational side, ever since the pioneer work by Kremer and Grest [39] on molecular dynamics of entangled polymers and seminal paper by Gao and Weiner [50] on the microscopic stress analysis in MD simulations, lots of progress have been made on the initial system preparation but the stress relaxation of entangled polymers in the linear regime has remained inaccessible. We may find the reason why reliable stress relaxation functions for entangled systems were not calculated years after Kremer-Grest and the Gao-Weiner papers. The typical stress-stress autocorrelation function is shown in Figure 3. All the stresses have relaxed at $t \approx 1$ since the amplitude of initial oscillations is significantly larger than the amplitude of all other processes. The log-log plot is much more revealing: it shows a total span of relaxation times of almost 8 decades, and this is just for a mildly entangled polymer [51].
Figure 3 Stress relaxation for the standard KG model, N=350. The inset shows the same data at an early time in log-linear scale [51].

Figure 3 illustrates two major difficulties in measuring the stress relaxation due to entanglements in molecular dynamics: 1) the time step has to be about $3 \times 10^5$ times smaller than the characteristic time, where entangled dynamics starts to appear. Since multi-chain simulations typically do not exceed $10^8$ steps, we have only 2.5 decades of "interesting" information to collect. 2) The value of the plateau modulus ($\approx 10^{-2}$) is almost 4 decades lower than the amplitude of stress fluctuations $G(0)$ due to bond length relaxation and other modes. Thus, the signal-to-noise ratio must be much higher than $10^4$ in order to obtain accurate information about the plateau modulus and the shape of the stress relaxation at long times.

A popular approach to circumvent this difficulty is to use non-equilibrium MD simulations, where a uniform shear is imposed on the simulation cell [52-56]. More recently, several groups have used equilibrium MD simulations to determine the stress autocorrelation function (SACF), which allows for the evaluation of time dependent shear modulus and the viscosity through the
Green-Kubo relationships [57]. For example, Sen et al. [58-61] calculated the SACF of the standard Kremer-Grest model and claimed to have observed a plateau for chain length N=120. Zhou and Larson [62] have also calculated the stress relaxation for one particular semi-flexible system. Complications are the limitation of time scale and computational size. Likhtman et al. [20, 51, 63, 64] used a new and efficient way to calculate a wide variety of correlation functions over many decades in time (up to 8) without significant additional Central Processing Unit (CPU) cost. Agrawal et al. [65, 66] applied a dynamic scaling factor to map the relaxation function to a real time scale. The uncertainties of this method have also been investigated, indicating that the largest component of the error is due to high-frequency bond vibrations characterized by very short relaxation times [59].

Detailed formula of the method will be given in Chapter 4, the storage and loss modulus can be computed by converting time-dependent shear modulus $G(t)$ into frequency domain after it has been fitted in Prony series with a two-step optimization method [67].

1.3.2 Calculation of Local Elastic Constants in MD Simulations

The overall mechanical performances of hard-soft copolymers are highly dependent on the constitutive relations of hard domains as well as the viscoelastic properties of the soft matrix. Since the hard domains’ $T_g$ is higher than room temperature and thus they remain in the “solid-like” state, elastic constants of such hard domains become significant both as inputs for a larger scale simulation models, and for the estimation and understanding of the interphase regions, which tells us how the hard domains interact with soft matrix.
To compute global elastic constants via MD simulations, two fundamentally different approaches, the deformation-based and the fluctuation-based methods, have been widely applied. The deformation-based method [68-70] is often used around $0K$. The elastic modulus is calculated from the slope of the stress-strain curve, in the same manner as for the macroscopic modulus. For the deformation-based technique [71], Mizuno et al. compared three different approaches (fully local approach, affine strain approach with local strain replaced by global strain, and frozen matrix approach) by using the same glassy materials [72, 73]. In order to suppress the fluctuation of stresses and strains, the simulation temperature is extremely low. However, this method still fails at a finite temperature due to fluctuations in stresses and strains at a nonzero temperature and is only valid for a static/quasistatic condition. To compute elastic constants while suppressing those fluctuations at finite temperatures, fluctuation methods are always employed [74-77]. In the strain-fluctuation technique, the isothermal elastic constant tensor can be obtained in terms of the Parrinello-Rahman (PR) strain fluctuation formula in an isothermal-isobaric (NPT) ensemble [78-80]. However, this method was found to converge slowly for many systems. More recently, the stress-strain fluctuation formula was explored based on statistical thermodynamics with much better convergence [81, 82].

While global stress-strain fluctuation methods have been used to calculate local elastic constants of hard polymer domains in hard-soft copolymers in previous studies [81-84], local fluctuation methods are rarely used because in order to apply the same methodology to local domains, the global stress and strain tensors must be replaced by local ones. Unfortunately, the definition and calculation of local strain remains an unsolved problem. In some literature, efforts have also been
devoted to obtaining the local elastic constants through the stress-fluctuation method[85-88], where the local material is hypothesized to undergo the same deformation with the global strains. The local elasticity tensor is thus obtained directly through the local stress and global strain instead of local strain. As a consequence, the results are approximations to the true local elastic constants. In addition, the local moduli of glassy polymers were also calculated by use of the stress-fluctuation technique [73]. However, this method fails to estimate the shear modulus when the material has large internal strains, especially for rubbery polymers.

Furthermore, for hard-soft copolymer systems, simply representing local strain by global strain does not work due to local heterogeneity. “Glass-like” hard domains coexist with the soft matrix, so the assumption of uniform displacement is not justified on molecular length scales. In addition, the non-affine or internal motion of particles gives rise to a decrease in the free energy after a homogeneous deformation. That non-affine part is particularly important in amorphous systems [68]. Therefore, local strain and local stress calculations are needed in addition to global ones. Falk and Langer [89] defined the effective local strain for each particle as the strain tensor that minimizes the non-affine character of the local displacements and that definition is employed in a series of papers by de Pablo et al [90-93]. In this dissertation, we will go through the stress-strain fluctuation method and also present the details of how we include the method from Falk and Langer [89] to define local strain. With that we provide a way to estimate the local elasticity tensor for polyurea systems with the information of local stress and local strain.

1.4 Effect of Interfacial Properties in Viscoelastic Relaxation Study using FEA

A critical jump is still needed before the material information collected from the CGMD model
could be utilized to predict macro-scale response of polyurea. Expanding the dimension of simulations in MD is straightforward, however, it is computationally impractical to model polymer systems with a molecular description, even if molecular-level details are represented by coarse-grained expressions, as in bead-spring models of polymers. An alternative way is to perform simulations using larger scale simulation methods like Finite Element Analysis (FEA) method.

FEA method is a general numerical method for obtaining approximate solutions in space to initial-value and boundary-value problems including time-dependent processes. It employs preprocessed mesh generation, which enables the model to fully capture the spatial discontinuities of highly inhomogeneous materials. It also allows complex and nonlinear tensile relationships to be incorporated into the analysis. Thus, it has been widely used in mechanical, biological and geological systems.

When carrying out experimental or computational assessments of the blast-mitigation efficiency of various elastomer-coating-based protection strategies, real-life target structures like building walls and vehicle body panels are typically replaced with thin/thick plate-like surrogate test-structures. Experimental and numerical work has been carried out to study the transient response of bilayer steel-polyurea plates under impulsive loads [8, 11, 94, 95]. In those studies, complex temperature-, pressure-, and rate- dependent constitutive models can be incorporated to study the dynamic response of the plates. For example, to study the micro/macro scale mechanical properties of polyureas, especially the energy storage and dissipation properties, experimental efforts and Finite Element Analysis (FEA) has been widely used. Amirkhizi et.al. [8] produced a model for the large deformation viscoelastic response of polyurea. The model incorporates the classical
Williams-Landel-Ferry (WLF) time-temperature transformation and pressure sensitivity, in addition to a thermodynamically sound dissipation mechanism. Grujicic et.al. [9] utilized that model for polyurea to investigate the blast-wave impact-mitigation ability of polyurea when used as a helmet suspension-pad material. Xue et.al. [96] presented a study of the impact and penetration of armor plates using a damage plasticity model for polyurea. Hyperelastic material models (Mooney-Rivlin material model) has also been employed by Mohotti [97]. However, in all these computational investigations, polyurea has been considered as a single-phase material, homogenizing the soft matrix, hard domains and interphase into one single effective material property. This homogenization process makes it difficult to study the enhancement mechanisms of hard domains in this material and to connect the tunable microstructural parameters with the overall response.

Generally, for polymer nanocomposites, it is clear that changes in the inherent properties of the matrix and the nanofiller and their relative volume fractions impact the composite response. A hidden level for performance optimization, however, lies in understanding and tailoring the matrix/filler interface. Depending on the dispersion state of the nanofiller and the interface area, the resulting interfacial region can be a critical and controlling component in polymer nanocomposites [98]. At the same time, direct characterization of the interphase domain is quite challenging experimentally. While some recent efforts have employed spectroscopic and nanoscale probe methods [99-102] to begin to gather experimental evidence on the changing properties in ~100nm near a nanofiller, a number of computational efforts have employed an inverse problem solution to find the interphase properties needed to match overall composite
response [103, 104].

In early work, homogenized analytical models were used to make predictions of interphase behaviors under simplified assumptions and constraints (e.g., Maxwell-Garnett Model[105], Bruggeman Model[106], Lichtenecker Model[107] and Hashin-Strikman[108] Model for nanodielectrics). Most of these analytical models use basic constituent information (volume fraction for example) to weight the contributions of individual constituents to interphases and apply this weighted-mixture of filler and matrix properties to estimate the bulk properties. With the rapid development of modern computation and the emerging numerical simulation tools such as ABAQUS, ANSYS or COMSOL, Finite Element simulations have provided the ability to consider the exact morphological information of microstructures, which leads to more accurate estimations of material properties.

Since effective interface model was proposed [109], scalability of the Finite Element approach has been considered to extend the capacity of the simulation to a larger volume of polymer nanocomposites [110]. Qiao and Brinson [111, 112] developed a 2D plane strain FEA model and studied the impact of interphase on the viscoelastic properties as well as thermal response of polymeric nanocomposites. In this model, FEA is performed on a representative volume element (RVE) with periodic structure (inhomogeneous distribution of particles inside a unite square). These results show that the distribution of particles has a significant impact on the interphase percolation and further influence on the viscoelastic properties of the bulk composites. Deng [113] implemented a similar plane stress model on the carbon-black/rubber composites with statistically reconstructed microstructures for viscoelastic modeling and gave an estimation of the thickness
and relaxation time of interfacial polymer in their systems. Similar FEA model is used in a data-driven approach to the virtual design of nanostructured polymers [114]. Xu et al. [115] developed a microstructure-based stochastic assembly approach to handle the problem of simulating very large Representative Volume Element (RVE) [116] and included the model in the workflow of a descriptor-based design methodology of a polymer nanocomposite systems [117].

In contrast, discrepancy between the numerical results and experimental data on a two-phase block copolymer indicates the presence of a third phase [118, 119], but including that intermediate phase in the computational model of hard-soft copolymer systems is still ongoing.

Like the strengthening mechanism of nanofillers in polymer nanocomposites [120-122], the inclusion of hard segments in TPUs not only results in increased stiffness, but the complex interaction of the elastic-like domains with the soft matrix significantly impact all physical properties of the system. The interactions between hard domains and their surrounding soft matrix alter the mobility of the polymer chains in both phases, resulting in an interphase area. Within this interphase area, material properties change gradually from soft matrix to hard domains when it approaches the boundary of hard domains. It’s well recognized that the effect of interphase region plays a key role in the overall properties of nanocomposites, especially viscoelastic responses [113, 123-125]. In contrast, unlike these widely noted concepts in polymer nanocomposite systems, discrepancy between the numerical results and experimental data on a two-phase block copolymer indicates the presence of interphase [118, 119], but including that intermediate phase in the computational model of hard-soft copolymer systems is still ongoing.
1.5 Dissertation Objectives

Previous sections highlighted the key motivation for this dissertation, as well as some of the fundamental physics and limitations to the current analytical models used to simulate the mechanics of hard-soft copolymer systems. The objective of this dissertation is to develop a multiscale framework to model the mechanical behavior of the thermoplastic polyurea and polyurethanes and to provide a better understanding and useful constitutive models that reflect microstructural compositions on the macroscopic observable properties. The study encompasses mapping from well-established and validated atomistic simulations to coarse grained MD simulations, and continuum length-scale simulations on interphase study between hard and soft domains, spanning over six orders of magnitudes of length. Accomplishment of this goal involves in four main tasks.

Figure 4 Scheme of the multiscale framework for modeling TPU.

1. Establishment of a CGMD model and mechanical response investigation of TPU.
the introduction of an energy factor to represent the interaction between hard beads, the bead-spring coarse-grained model is used to represent the hard-soft copolymers. Based on physical properties such as temperature dependent densities and glass transition temperatures from well-established and validated atomistic simulations, accurate input parameters for the CGMD models are derived and results from CGMD models can also be fitted and scaled from Lennard-Jones units to the real units. With the CGMD model, the critical information regarding the phase-separation microstructure and its evolution at various conditions can help us further understand the effect of composition and attraction of hard beads on the morphology of copolymers. To study the effect of temperature, strain rate and pressure on shear resistance of polyurea under pressure, shear-under-pressure tests of polyurea systems need to be conducted to answer questions in a series of experiments on that.

2. Calculation of mechanical properties of soft and hard domains using CGMD model. Viscoelastic properties of the soft domains and elastic constants of hard domains are needed as inputs for our macroscale model because soft matrix are rubbery and hard domains are regarded as in their glassy state at room temperature. Stress relaxation behavior of polymers is hard to simulate for its long-time range. Stress autocorrelation function is used in this dissertation to calculate the linear viscoelastic behavior of soft matrix and hard-soft copolymer systems. In addition, to compute truly local elastic constants of hard domains, we need to define both local stress and local strain. Only after that can we compute the truly local constants with stress strain fluctuation method at room temperature.

3. Derivation/Definition of geometrical and material inputs for three phases (soft, hard
and interphase) in FEA model and investigation of the interphase effect. To run FEA simulations of polyurea systems with more than one phase, both geometrical and material inputs are needed for these phases. The geometrical structure in this dissertation is derived from the 2D AFM phase image where the phase image is binarized into two separate phases and gradient interphase layers are added. The viscoelastic property of soft matrix is obtained from the combination of DMA data and CGMD simulation results. Interphase properties are assumed to be similar with that of the soft matrix and are a shift to the low frequency range. The shifting factor is dependent on the distance from hard domains. With both the geometry and the properties determined, an FEA model can be built and used to study how interphase impacts the copolymers’ overall viscoelastic response.

4. Identification of interphase feature importance in affecting the copolymer’s mechanical response. There are several interphase features that are important in determining polyurea’s overall viscoelastic response. For example, interphase thickness, interphase property distribution across that thickness and volume fraction of interphase layers. Apart from that, volume fraction and modulus of hard domains also play a role. To relate those features with viscoelastic responses, we need a ranking algorithm to give a quantitative indication. Random forest algorithm is chosen to do that after the interphase is represented with a vector and ten variables are summarized from that vector to represent interphase features. With ten features and four indicators of viscoelastic response (tan δ peak decrease, tan δ peak shift, instantaneous storage modulus and long-term storage modulus), we run the ranking algorithm and present the feature significance.
1.6 Dissertation Structure

The remaining structure of this dissertation provides a detailed description of methodologies in Chapter 2. It includes how we map from atomistic simulations to coarse-grained MD models, how we fit the dynamic shear modulus with Prony series and an in-depth look at the stress strain fluctuation method. This chapter is to ensure the reading has the minimum background to follow the presented work. Chapter 3 presents the morphology of different systems and their mechanical responses under tension, which is followed by their shear resistance under pressure and the influence of several factors on this shear resistance. Chapter 4 focuses on the calculation of mechanical properties for each phase, including calculation of viscoelasticity of the soft matrix using stress auto correlation function and computing elastic constants of the hard domains via fully local stress strain fluctuation method. In Chapter 5, we built up a finite element framework to simulate linear viscoelastic response of hard-soft block copolymers by introducing gradient interphase layers between hard and soft phases. Then we explore how the properties, extent and connectivity of this interphase domain affect the copolymers’ viscoelastic behavior. Details of how we get both geometry and material inputs for the FEA model are presented, as well as qualitative analysis on the effect of interphase properties. Following that, a quantitative analysis is presented by ranking the importance of each interphase property feature in determining the responses. This understanding is valuable toward fundamental understanding of the underlying physics in enhancement mechanism brought by hard domains in hard-soft copolymer systems. Finally, in addition to a summary of contributions, a conclusion detailing the completed objectives is provided in Chapter 6, followed by an outlook into the future work.
Chapter 2  Computational Methodology

In this chapter, we first build a coarse-grained molecular dynamics (CGMD) model based on the previous all-atom molecular dynamics model. The coarse-grained polymer model can be described as beads interconnected with springs, i.e., a bead-spring model suggested by Kremer and Grest [39, 126], which has been widely employed as a generic theoretical model in the realm of polymer physics [31, 44, 45]. After introducing the coarse-grained model with the parameters used and the preparation of hard-soft copolymer systems, we present a two-step optimization method to fit the time dependent shear modulus with Prony series, and the stress strain fluctuation method to calculate elastic constants in molecular dynamics simulations.

2.1  Atomistic Simulations of Polyurea

The goal of the atomistic simulations is to obtain various physical parameters of bulk polyurea for parameters in coarse-grained models. To achieve that, three polyureas with different numbers of repeating units (\( \text{\(\text{C}_2\text{H}_8\text{O}_n\)} \) unit) are considered, i.e., \( n = 7, n = 14, n = 28 \). Note that each chain only contains one monomer due to computational time limitations with current computer resources. Periodic boundary conditions are applied in three directions and the computational unit cell is shown in Figure 5. Polymer consistent force field (PCFF) functional forms are used for various bond and non-bond interaction energies. Each term in the force filed stands for the bond, angle, torsion and relevant coupling interactions as well as non-bond potentials, respectively. PCFF is a set of force field potentials which are derived through \textit{ab initio} calculations and has been applied to condensed matter extensively.
All MD simulations are conducted using the LAMMPS software package [127]. NVT and NPT statistical ensembles are adopted, implemented by Nose-Hoover thermostat [128] and Anderson pressostat. Anderson algorithm is used to generate the equilibrium states. Time step is set as 1 fs and the external pressure is fixed as 0. The velocity-Verlet algorithm is chosen to integrate the equations of motion.

To equilibrate each individual system at zero pressure, we simulate the system for 10 ns in NPT ensemble after initial energy minimization procedure. All the chains move at least 2 $R_g$, the radius of gyration. The next step is to quench the systems at a rate of 0.1 K/ps for desired temperatures. Once the polymer is quenched to each particular temperature, it is relaxed under constant temperature and zero pressure for 5 ns.
Figure 6 Density of four different polymers with respect to temperature.

The temperature dependent densities for these hard-soft block copolymers are calculated, as shown in Figure 6. As expected, the hard segments tend to aggregate together which results in the increased density. Smaller number of repeating unit ($C_2H_8O$ unit), corresponding to higher concentration of hard segments, could lead to a further increment of the density. It is found that all the densities decrease linearly with temperature but with two distinct slopes. The abrupt change of densities indicates the glass transition temperature, which suggests that $T_g$ s of these models vary from 241K to 414K. In addition, the $T_g$ s are above and below room temperature for all-hard polymer and polyurea, respectively, consistent with the experimental expectation. Higher concentration of hard segments reveal that more energy is required to transform these polymers from glassy state into rubbery state, i.e., higher $T_g$.

In this subsection, we aim at investigating the impact of hard segments on the glass transition temperature that is an important descriptor of the thermo-mechanical performance of polymeric
materials. The density evolutions have already shown the existence of \( T_g \) for these four hard-soft copolymers. Such macroscopic observable variation is controlled by intrinsic movements of the polymer chains, which is determined by the interaction between atoms and ions. In order to discover the role of each potential in the glass transition, we compare the results between bond, angle, improper, dihedral, Vander Waal and Coulombic potential energies. Energies from dihedral and Vander Waal potentials exhibit the similar behavior as the density evolution, as shown in Figure 7 (e)-(f). The glass transition temperatures obtained through linear fitting from them are almost the same. Furthermore, the Vander Waal and dihedral potential energies increase linearly with increasing temperature above and below \( T_g \). These results agree well with the work from other references. On the contrary, no sudden change is observed in bond, angle and improper potential energies (Figure 7 (a)-(c)). This is because the glass transition is a phenomenon related to segmental relaxations restricted by intermolecular environment rather than the intramolecular changes, and the relative movements between different chains are controlled by non-bond potential. This agreement helps validate our models and simulations.
Figure 7 a) bond, b) angle, c) improper, d) Coulombic, e) dihedral and f) Vander Waal interaction energies versus temperature for these four copolymers. Only Dihedral and Vander Waal energies exhibit the glass transition behavior.
2.2 Mapping to Coarse Grained Models

As we mentioned above, the goal of atomistic simulation is to obtain the potential parameters of the CG model for polyurea. A bead-spring model suggested by Kremer and Grest [39, 126] is employed, which has been widely used as a generic theoretical model in the realm of polymer physics. The first step is to estimate the average bond lengths and angles, i.e., the locations of peaks in distribution functions. Due to the general rule for the CGMD simulation, CG beads are relatively hard, thus automatically preventing bond crossing. This implies an upper limit on the number of atoms that can be lumped together.

Figure 8 Five different beads are representing a monomer of polyurea.

Table 1 Functional group and mass of each CG bead from Figure 8 for polyurea

<table>
<thead>
<tr>
<th>CG Bead</th>
<th>Functional Group</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td></td>
<td>58.0396</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59.0475</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>83.111</td>
</tr>
<tr>
<td></td>
<td></td>
<td>84.119</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>120.1074</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>104.108</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>72.1066</td>
</tr>
</tbody>
</table>
The polyurea is first coarsely grained as shown in Figure 8. Five kinds of CG beads with the mass range from 60~120 are used to represent the monomer of polyurea. The details of each CG bead are described in Table 3. By analyzing the polymers based on the selection of CG beads, we find that there are overall 7 different types of bond and 7 types of angle, respectively, as listed in Table 1.

After investigating the coordinates of each atom of the polymer melts, the distribution functions for bond and angle are computed, as displayed in Figure 9. The average bond distances vary from 4Å to 6 Å, depending on the size and mass of bonded beads. From Figure 9-(b), it is obvious that some angle distributions exhibit more than one peak. In this case, we only consider the largest peak as the initial guess of the equilibration value. Finally, the hard segment is lumped into two hard beads and soft segment into 8 beads for the polyurea (n is 14 in \( C_2H_8O_n \)), and in real cases, we have three polyurea with n to be 14, 9 and 3 respectively. They correspond to three kinds of coarse grained chains (H2S8, H2S5 and H2S2), which will help us to study the effect fraction of hard beads.

![Figure 9 Distribution functions of 7 bonds and angles for CG model of polyurea.](image)
2.3 Coarse-Grained Molecular Dynamics Techniques

For the generic coarse-grained bead-spring polymer model used here, the model can be described as beads interconnected with springs, i.e., a bead-spring (coarse-grained) model suggested by Kremer and Grest [39, 126]. In this model, a polymer is composed of coarse-grained beads with the same properties. In order to simulate the mechanical responses of elastomers such as polyurea and polyurethane that are of interest, we extend this model by distinguishing the beads with different properties. In our model, the beads are classified as shown in Figure 10 where H and S denote hard and soft beads, respectively. The model with all soft beads is also investigated as the control sample. We prepare the system by randomly placing 500 chains in a cubic box with 100 beads in each chain using a non-reversal off-lattice random walk. Periodic boundary conditions are applied in three directions. To simulate the stiffness enhancement of hard segments, we take the equilibrium all-soft-bead structure as the base model and then create the new hard-soft structure by replacing some of the soft beads with hard ones in regular patterns (Figure 10).

The core of MD method is the interatomic potential. For the coarse-grained polymer, only bond and non-bond potentials are adopted to describe the interactions between the beads based on morphology. Here, we need to assign the potentials for hetero- and homo-species beads to understand the behaviors of both soft and hard/soft materials. For simplicity, the all soft-bead material is considered as the benchmark. A reduced unit system is used for all the quantities expressed, where the fundamental units are $\sigma = \sigma_{S-S} = 1$ for length, $\varepsilon = \varepsilon_{S-S} = 1$ for energy, $m = m_{S-S} = m_{H-H} = 1$ for mass, and $k_B = 1$ for the Boltzmann constant. Other units of interest can be derived from these fundamental units such as temperature can be expressed in $\varepsilon/k_B$, pressure
in $\varepsilon/\sigma^3$, and time in $\tau = \sqrt{m\sigma^2/\varepsilon}$. The subscripts $S$ and $H$ represent the soft and hard beads, respectively. The non-bonded interaction is modeled using a standard 12-6 Lennard-Jones (LJ) potential with a specific cutoff distance $R_c = 2.5\sigma$:

$$V_{LJ} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

(1)

where $r$ is the distance between two non-bonded beads. Both repulsive and attractive forces are included in this non-bonded potential due to the cutoff distance. This force is very important when calculating the mechanical properties. For the classical Kremer and Grest (KG) model, only a repulsive force is employed, i.e., $R_c = 2^{1/6}\sigma$. Such model is close to an athermal model of polymer, lacking the ability to predict the glass transition driven by temperature. Furthermore, some simulation results reveal a negative thermal expansion coefficient without attraction.

For the bonded potential, the springs connecting the beads act as a covalently bonded backbone in the polymer chain. An unbreakable bond with finite extensible nonlinear elastic (FENE) potential is used in the simulations:

$$V_{FENE} = -0.5KR_0^2 \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right] + 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + \varepsilon$$

(2)

where $K = 30\varepsilon/\sigma^2$, $R_0 = 1.5\sigma$ is the maximum possible length of the bond. Note that the first term is attractive, and the second Lennard-Jones term is repulsive with a smaller cut-off distance $R_c = 2^{1/6}\sigma$. 
Besides the potentials for soft beads, the interactions between hard beads and hard-soft beads are also required. Like the all-soft-bead material, these potentials can also be divided into two parts: bonded and non-bonded potentials. As presented in the atomistic simulation results and shown in our previous study [32], the non-bonded potential dominates the mechanical properties. Therefore, the bonded potentials are assumed to be the same between all beads. The structure of hard-soft polymer can be approximately described by a modified non-bonded interaction represented by a Lennard-Jones potential with appropriate interaction parameters. For convenience, we only vary the energy factor. The parameters for soft and hard beads respectively are $\sigma_{H-H} = \sigma_{H-S} = \sigma_{S-S} = 1$, $\epsilon_{H-H} = \lambda \epsilon_{S-S}$, and $\epsilon_{H-S} = \sqrt{\epsilon_{H-H} \epsilon_{S-S}}$. Large $\lambda$ values designate stronger attractive forces between hard beads. To study the effect of hard-bead fraction, we have coarse grained chains H2S8, H2S5 and H2S2, corresponding to the three commonly used polyurea formulations PU1000, PU650, and PU250, respectively (repeating units in soft domains $(C_4H_8O)_n, n = 14, 9, 3$), as shown in Figure 10.

Figure 10 Schematic representation of the approximation of the hard and soft phases for hard-soft copolymers.
Detailed preparation of the system can be found in our previous paper [32]. In brief, the system is first equilibrated at a high temperature (above $T_g$ of both hard and soft domains) and then quenched to the desired temperature, which is lower than $T_g$ of the hard domains. Therefore, the quenching and equilibration process at low temperature results in a self-assembled hard-domain network, with hard beads gathering together to form hard segments. Additionally, for a fixed temperature, large $\lambda$ values make the system prone to have crystallized hard segments. The MD simulations are conducted by using the LAMMPS software package [127]. In our simulations, the NVT and NPT statistical ensembles are adopted, implemented by the Nose-Hoover thermostat and Anderson and Parrinello-Rahman (PR) pressure statistics. The Anderson algorithm is used to generate the equilibrium state while PR method is used for the calculation of elastic modulus. The time step is set as 0.005$\tau$. The velocity-Verlet algorithm is chosen to integrate the equations of motion.

### 2.4 Two-Step Optimization Method for Prony Series

The viscoelastic properties of copolymers are computed using equilibrium MD simulations performed in the canonical (NVT) ensemble. Specifically, the time-dependent shear modulus is calculated from the stress autocorrelation function (SACF), which will be explained in detail in Chapter 4 to make the discussion consistent. Here we will explain how we describe the obtained time dependent shear modulus using a Prony exponential series expansion,

$$G(t) = G_0 - \sum_{i=1}^{N} G_i \left[1 - e^{-t/\tau_i}\right]$$

where $\tau_i$ are the relaxation times, $G_0$ is the instantaneous modulus, and $G_i$ are the Prony
coefficients. We will also explain how we determine the Prony coefficients by fitting data from MD simulations. Suppose there are \( N \) exponential terms in Eqn. (3), overall \( 2N+1 \) parameters need to be evaluated. One approach for obtaining these parameters is to consider the estimation as an optimization problem [129-131]. Clearly, this is a multi-parameter optimization problem. To this end, many efforts have been devoted to obtaining these parameters. However, most of them are based on the traditional optimization techniques, which utilize deterministic schemes to move from one point to another in the searching space, yielding locally optimal solutions. For example, multidata method [132] and improved versions [133, 134] adopt the linear least square solver (LLSS) to compute \( G_i \) by assuming the set of relaxation times \( \tau_i \). Under such a condition, the LLSS becomes possible and the total unknowns have been reduced to \( N \). Nevertheless, these approaches yield a ‘secondary-optimal’ solution due to the pre-defined \( \tau_i \). Other attempts have been made to impose nonlinear least square solver without such constraints [135, 136]. In this case, ill-condition and divergence could occur if the initial guesses are far from the optimal values. Such drawback limits their applications in multi-dimensional optimization problems.

In principle, the optimization progress could be accomplished readily if the bound of each parameter (\( \tau_i, G_i, \) and \( G_0 \)) is known beforehand. For \( G_0 \), the effective bound could be defined as the data either in high frequency domain or in initial time domain within a small variation. For \( \tau_i \), one can simply choose the experimental test duration as the bounds for all the \( \tau_i \). But this may lead to a singular matrix in LLSS if two \( \tau_i \) are quite close. Therefore, a unique bound for each \( \tau_i \) is essential. As inspired by [133], the appropriate range of each \( \tau_i \) could be assumed as the interval
of test duration at log-scale divided by the number of exponential terms ($N$). For instance, if the test time is from $10^{-3}$ to $10^4$ s and $N$ is taken as 7, the bound of each $\tau_i$ could be set as $[10^{i-4}, 10^{i-3}]$. However, it’s generally impossible to obtain the valid range for $G_i$, which may cover several orders of magnitude. For clarity, we denote the $\tau_i$ and $G_0$ as one set (SET-I) and $G_i$ as the other set of parameters (SET-II). To evaluate these two sets of parameters, we decouple this problem and divide it into two separate issues. Accordingly, two optimization methods, particle swarm optimization (PSO) and constrained linear least square solver (CLLSS), with two distinct target functions are employed to satisfy different requirements. Since the bounds of SET-I could be pre-estimated, it’s appropriate to utilize PSO method to select and to optimize those parameters. Due to the essence of (3), where the dynamic shear modulus $G(t)$ is a linear function of $G_i$, one can use CLLSS to determine $G_i$ directly once the $\tau_i$ and $G_0$ are known.

Recently, particle swarm optimization (PSO) [137, 138] has drawn increasing attention as a novel population-based optimization technique. It can determine many adjustable parameters simultaneously by simulating the animal social behaviors, e.g. birds flocking, fish schooling and insects herding. Due to its simple concept and fast convergent speed, it has been widely applied to many areas such as power system, structural damage identification, nonlinear system identification, steel annealing process, and magnetoencephalography.

In the PSO methodology, each individual (called particle) represents a potential solution without mass and volume, and flies within the searching space to seek the food (optimum). Suppose $\mathbf{x}_j(t) = (x^1_j(t), x^2_j(t), ..., x^D_j(t))$ ($D$ denotes the dimension of problem space) is the position vector
of the \( j^{th} \) particle at generation \( t \), then it flies with the following manner

\[
x^k_j(t+1) = x^k_j(t) + v^k_j(t+1),
\]

(4)

where the symbol \( \vec{v}_j(t+1) = (v^i_j(t+1), v^2_j(t+1), ..., v^D_j(t+1)) \) represents the velocity of particle \( j \) at time \( t+1 \), and is updated by

\[
v^k_j(t+1) = wv^k_j(t) + c_1r_1(p^k_j(t) - x^k_j(t)) + c_2r_2(p^g_k(t) - x^k_j(t)),
\]

(5)

where \( \vec{p}_j(t) = (p^1_j(t), p^2_j(t), ..., p^D_j(t)) \) is the \( j^{th} \) particle’s best position, and \( \vec{p}_g(t) = (p^1_g(t), p^2_g(t), ..., p^D_g(t)) \) represents the best position found by the entire swarm. In other words, \( \vec{p}_j(t) \) and \( \vec{p}_g(t) \) are the locally and globally optimal solutions, respectively. Inertia weight \( w \) is a positive number within 0 and 1. Cognitive learning factor \( c_1 \) and social learning \( c_2 \) are known as accelerator coefficients, \( r_1 \) and \( r_2 \) are two random numbers generated with uniform distribution within \((0, 1)\). To keep the stability for PSO algorithm, a pre-defined velocity threshold \( v_{\text{max}} \) is used to limit the moving size of velocity vector such that

\[
|v^k_j(t+1)| \leq v_{\text{max}}.
\]

(6)

The reflected boundary condition is applied to upper and lower bounds to ensure the \( x^k_j(t+1) \) stays within its pre-defined range. Note that the PSO method is only used to determine parameters \( \text{SET-I} \). Thus, each particle here means one set of \( \tau_i \) and \( G_0 \).

Optimization Procedures
Because two optimization methods are adopted, we need to define two objective functions for PSO and CLLSS, respectively. For convenience, the objective function could be defined as either absolute error or relative error, i.e.,

\begin{equation}
\Pi(x) = \sum_{i=1}^{N} w_i \left[ \frac{f_i(x)}{y_i} - 1 \right]^2, \quad \Pi(x) = \sum_{i=1}^{N} w_i \left[ f_i(x) - y_i \right]^2.
\end{equation}

where $x=(x_1, x_2, \ldots, x_M)$ represents a set of candidate parameters ($\tau_i$, $G_i$ and $G_0$), $f_i(x)$ could be the dynamic shear modulus, storage modulus or loss modulus calculated by the optimization with the parameter set $x$. The $y_i$ is the corresponding value of the same modulus from the experimental measurement. The weighting factor $w_i$ is a positive number selected based on the importance of the particular property. The purpose here is to find a particular $x_0$ so that $\Pi(x_0) \leq \Pi(x)$ for all $x$ in the searching space. We need to point out that the choice of the weighting factors are somewhat subjective. One can recruit high weighting factor for the properties that are most relevant to their interests. Here, all the weighting factors are assumed to be the same for simplicity.

To start the optimization, $G_0$ and $\tau_i$ of each particle are first designated with random values within the bounds as the initial guess by PSO algorithm. After that, CLLSS is carried out to compute $G_i$ with the initial set of parameters ($G_0$ and $\tau_i$) based on a particular target function, e.g., Eq. (7). This is the first iteration of those parameters and $f_i(x)$. The next set of $G_0$ and $\tau_i$ are then selected using the PSO algorithm based on its target function in Eq. (7). The above procedures are repeated until the convergence criterion is met. In brief, the PSO algorithm is to generate and to update $\tau_i$ and $G_0$ while the objective of CLLSS is to find the $G_i$ that make $\Pi$
reach the minimum value, which requires $\frac{\partial \Pi}{\partial G_i} = 0$. Note that CLLSS is utilized to force all the $G_i$ to be positive. Figure 11 shows the flow chart of the optimization procedure.

Figure 11 Illustration of the optimization procedure

To illustrate the feasibility of this approach, we take the data of tensile modulus[133] as an example to show the accuracy of this two-step optimization method. Figure 25 shows that there is a very good agreement between the raw data and the fitting result.
Figure 12 Data for tensile modulus of polyisobutylene at \(25^\circ C\) from Ref[133]. The Prony series fitting is obtained using the two-step optimization method.

2.5 The Stress Strain Fluctuation Method

There are several ways to calculate elastic constants depending on the fluctuation techniques in various isothermal-isobaric (NPT) ensembles. For example, the isothermal elastic constant tensor can be obtained in terms of the PR strain fluctuation formula [78],

\[
C_{ijkl} = \frac{k_B T}{\langle V \rangle} \left[ \langle \varepsilon_{ij} \varepsilon_{kl} \rangle - \langle \varepsilon_{ij} \rangle \langle \varepsilon_{kl} \rangle \right]^{-1}
\]  

where \(\varepsilon_{ij}\) is the strain tensor, \(\langle V \rangle\) is the average volume of the system, \(k_B\) is the Boltzmann constant, \(T\) is the temperature, \(\langle \cdot \rangle\) denotes the ensemble average. \(i, j, k, l\) The indices represent the Cartesian coordinates in three dimensions and run from 1 to 3. The strain tensor is given by

\[
\varepsilon_{ij} = \frac{1}{2} \left[ \langle h \rangle_{ik}^T ~ h_{kl} h_{mn} \langle h \rangle_{mj}^{-1} - \delta_{ij} \right]
\]
$h$ is the scaling matrix $h = \{\hat{a}, \hat{b}, \hat{c}\}$, where $\hat{a}$, $\hat{b}$, and $\hat{c}$ are three basis vectors describing the size and shape of the simulation box. The matrix $\langle h \rangle$ is the average frame of the system as the reference state. $h^{-T}$ is the inverse of the transpose of $h$, and $\delta_{ij}$ is the Kronecker tensor. The conventional suffix notation is used, where repeated suffixes indicate summation over the values of 1, 2, 3 unless otherwise stated.

The strain fluctuation method is found to converge very slow for our system. In Refs [84, 139], the stress strain fluctuation formula is used to estimate the adiabatic and isothermal elastic constants in NPH and NPT ensembles, respectively. In that method, the global elastic constants are computed through

$$C_{ijkl} = \langle \sigma_{ij} \varepsilon_{mn} \varepsilon_{kl} \rangle^{-1}$$

where the bracket $\langle \rangle$ denote the ensemble average. The global strain $\varepsilon_{ij}$ is calculated with Eqn. (9) with the scaling matrix $h$ fixed. The global stress $\sigma_{ij}$ and of a given simulation system are given by

$$\sigma_{ij} = -\frac{1}{V} \left[ \sum_{\alpha} m_{\alpha} \left( \frac{p_{\alpha}}{m_{\alpha}} \right)_{i} \left( \frac{p_{\alpha}}{m_{\alpha}} \right)_{j} - \sum_{\beta > \alpha} \frac{\partial U}{\partial r_{\alpha \beta}} \left( \frac{r_{\alpha \beta}}{r_{\alpha \beta}} \right)_{i} \left( \frac{r_{\alpha \beta}}{r_{\alpha \beta}} \right)_{j} \right],$$

where $V$ is the volume of the system. $m_{\alpha}$ and $p_{\alpha}$ are the mass and momentum of the $\alpha$ th atom, respectively. $U$ is the potential energy and assumed as a function of atomic distance. $r_{\alpha \beta}$ is the distance between the atoms indexed as $\alpha$ and $\beta$. Global strain is as in Eqn. (9) with the scaling
matrix \( h \) fixed. Eqn. (10) has been proven to be more efficient than Eqn. (8) for the improved convergence property.

Definition of local stress and local strain will be given in Chapter 4 and we utilize the stress strain fluctuation method with local stress and local strain to calculate the local elastic constants. It should be noted that, Eqn. (8)(9)(10) assume the validity of linear elasticity, where strains and strain fluctuations are sufficiently small, hence the elastic constants of the stiff or soft materials may be inappropriately calculated with those formulas. In order to extend their application fields, the elastic bath method can be used to facilitate fast and accurate calculation of elastic constants.

2.6 Summary

In this chapter, the process of how we map from atomistic MD model to the CGMD model is presented, followed by the two-step optimization method to fit time-dependent shear modulus with Prony series. The former part should clarify terms when we start from the CGMD model at the beginning of Chapter 3. In addition, the fundamental principles that make up the stress strain fluctuation method in MD simulations is also presented to provide a general knowledge needed to follow the studies presented in Chapter 4.
Chapter 3  Morphology and Mechanical Response of Polyurea Calculated through Coarse-Grained MD Simulation

In this chapter, we present the morphology of hard-soft copolymer systems with different composition and interaction between hard and soft beads as well as their mechanical responses under tension. Following that is their shear resistance under pressure and the influence of several factors on this shear resistance. Factors such as applied pressure, shear strain rate, temperature, fraction of hard segments and interaction between hard beads are discussed in terms of influence on the final shear resistance. Our numerical experiments show that pressure is the most crucial factor in shear-under-pressure tests, with larger pressure leading to higher shear resistance of the copolymers.

3.1 Microstructure and Morphology

The material properties of polyurea are highly related to their microstructures, including both molecular composition and interactions between different components. First, we show the effect of hard-hard interactions on microphase separation for a fixed fraction of hard beads. Presented in Figure 13 are the representative configurations of H2S8 block copolymers with three different energy factors at a temperature of $T = 0.55\varepsilon / k_B$. $T = 0.55\varepsilon / k_B$ corresponds to room temperature in real units and will be presented as $T = 0.55$ in the rest of the dissertation. Green and red beads represent soft and hard beads, respectively. Although all copolymers manifest microphase separations into hard domains surrounded by soft matrix, their morphologies differ significantly. A small energy factor ($\lambda = 2$) yields small segregated hard domains, whereas hard beads self-
assemble into thick and strongly segregated hard domains in the case of a larger energy factor ($\lambda = 5$). This difference arises because large $\lambda$, corresponding to higher binding forces between hard beads, significantly restrains their interbead and intrabead movement. Consequently, the hard segments from the same and different chains both participate in the formation of hard domains.

![Figure 13 Snapshots of three hard-soft block copolymers](image)

Figure 13 Snapshots of three hard-soft block copolymers, showing microphase separation of H2S8 with energy factor (a) $\lambda = 2$, (b) $\lambda = 3$, (c) $\lambda = 5$. As in Figure 10, green and red beads correspond to soft and hard domains, respectively. Snapshot size is 40nm×40nm.

![Figure 14 RDFs](image)

Figure 14 RDFs between hard-hard beads at temperature 0.55 for four copolymers with different energy factors.

After equilibration at temperature $T = 0.55$, we characterize three systems with radial distribution functions (RDFs), $g(r)$ in Figure 14 and find evident structural differences. Hard domains of systems with higher energy factors exhibit a more “glass-like” structure as evidenced
by $g_{H-H}(r)$ curves showing more pronounced short-ranged peaks (as in $\lambda = 4$ and $\lambda = 5$ cases in Figure 14). This result is in agreement with the morphologies observed in Figure 13.

Figure 15 Snapshots of three hard-soft block copolymers with a constant energy factor $\lambda = 5$. Microphase separation of (a) PU1000, (b) PU650, (c) PU250 at T=0.55. Snapshot size is 40 × 40 nm.

Figure 16 500 nm × 500 nm tapping mode AFM phase images of (a) P1000 and (b) P650 polyurea in which the hard domains appear as bright regions. Reprinted with permission from Castagna et al., Macromolecules, 2012, 45(20), 8438-8444. Copyright 2012 American Chemical Society [140].

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Simulations with the same interactions between different components result in the morphologies displayed in Figure 15. The composition changes from H2S8 to H2S5 and finally to H2S2, with correspondingly increased density of hard beads. At the same time, ribbon-like hard domains become less dispersed and the aspect ratio of each single hard domain decreases. The AFM phase image in Figure 16[140] shows a similar trend for PU1000(H2S8) and PU650(H2S5) cases. Particularly, the volume fraction of hard beads is so high for the PU250(H2S2) case that it is impossible to define two distinct phases. This mixed state of PU250 in Figure 15 agrees with the experimental observation that PU250 polyurea does not exhibit discernible phase separation.

3.2 Mechanical Response under Tension

For the above three systems with various energy factors, we pick two (PU1000 and PU650) with two energy factors (λ = 2 and λ = 5) and present their stress-strain responses under tension at a temperature of \( T = 0.55 \). Since we have shown in our previous study [32] that the strain rate influences the mechanical response significantly, we choose a single strain rate (10^{-5} \tau^{-1}) to illustrate how the composition and energy factor in the hard-soft copolymers affect the mechanical behavior.
Figure 17 Tensile stress-strain curves at $T=0.55$ and a strain rate of $10^{-5} \text{ s}^{-1}$ for two PU configurations and two energy factor $\lambda$. (b) is the zoom-in for green box in (a). PU650 is represented by the H2S5 model, while PU1000 is simulated as H2S8.

As shown in Figure 17, the initial modulus is dependent on both the concentration and attraction of hard segments. Materials with small $\lambda$ ($\lambda = 2$) demonstrate “liquid-like” behavior with much lower stiffness than those with large $\lambda$ ($\lambda = 5$). PU650-$\lambda = 5$ and PU1000-$\lambda = 5$ can sustain higher loads because large $\lambda$ results in stiffer hard domains that increase overall strength. Note that stress remains at a constant low level for small-$\lambda$ cases after the initial increase, while it experiences a second rise with a reduced slope for large-$\lambda$ systems. Moreover, strength of PU650 is always higher than that of PU1000 with the same $\lambda$, which is the result of a larger volume fraction of hard segments in PU650. We know from morphology study of polyureas that morphology reflects both the volume fraction effect and the energy factor effect. Therefore, the morphology determined by interaction between hard beads and volume fraction of hard beads is critical for the response to large deformation. This information is critical for the molecular design of hard-soft copolymers.
3.3 Shear Resistance under Pressure

Shear resistance under pressure is of major importance in polyurea coating applications because such loading conditions are encountered when polyurea coatings are subjected to impact by high-velocity projectiles. Motivated by promising experimental results [14, 27-30], we conduct the following simulations to study the copolymers’ shear resistance under pressure and to discover the most important factors that determine this critical material property. In our simulations, PU1000 is used for comparison with experimental results. After the structure is quenched to a desired temperature and fully equilibrated, compression deformation is first applied. Subsequently, the system experiences shear deformation under various pressure conditions. Detailed discussion regarding the influence of several parameters on shear resistance are given in the following subsections. These factors include pressure, shear strain rate, temperature, fraction of hard segments and interaction between hard beads ($\lambda$). These results demonstrate the importance of microstructure on macro-mechanical responses in such systems and serve as a reference to guide interpretation of results from pressure shear plate impact (PSPI) experiments. Only in this part we use real units to present the results concerning pressure and shear strain rate to make a direct comparison with PSPI experiments. The scaling parameters are $\alpha \approx 7.45 \times 10^{-21} J$ and $\beta \approx 5 \times 10^{-10} m$, where $\varepsilon_{\text{real}} = \alpha \varepsilon$ and $\sigma_{\text{real}} = \beta \sigma$. 
3.3.1 Pressure

![Graph](image)

Figure 18 (a) Shear stress strain curves under pressure via MD simulation for $\lambda = 2$ at $T=0.55$ and strain rate of $1 \times 10^{-6} \text{ s}^{-1}$ as a function of pressure; (b) comparison of shear resistance between CGMD (solid lines from (a)) and experimental results (lines with markers) under the same conditions, with the same color corresponding to similar pressure level [30].

The copolymer has very low shear stiffness under pure shear, whereas both the initial shear modulus and shear strength increase with increasing applied pressure, as depicted in Figure 18-a. During the simulation of the compression prior to applying shear conditions, we observe that the simulation box becomes smaller and hence the decreased volume leads to a denser material. Therefore, the stiffening effect is the result of densification, which brings additional vitrification. These results agree with PSPI experiments [27-30], which show similar effects of pressure on the shear resistance. Figure 18-b gives a direct comparison between the experimental and MD simulation results. Since the CGMD model is a simplified representation of the copolymer system and only captures coarse structural features, we do not expect to match those results perfectly. Our goal is to verify the model and to probe the mechanism by which each factor influences the shear resistance. The good qualitative agreement between experiments and our simulations indicate that the physics of the former is reasonably represented by the latter.
Figure 19 (a) Initial shear moduli and ultimate shear strength of H2S8 ($\lambda = 2$) are plotted w.r.t. applied pressure. (b) Volume change of simulation box w.r.t. applied pressure.

To further discuss the pressure effect, we plot the pressure-dependent initial shear moduli and shear strength in Figure 19-a. Clearly, both of them exhibit a bilinear tendency. Specifically, when pressure is below 0.4 GPa, both initial shear moduli and shear strength respond in a linear way, followed by a subsequent linear regime at higher pressures but with reduced slope. Figure 19-b presents the volume reduction of the simulation box under various pressure levels. The similar trend in shear strength and volume reduction indicates that the compaction resulting from the
application of pressure can greatly improve the shearing resistance, leading to a higher sustainability to shear loads. In addition, this densification reduces above the threshold pressure of about 0.4 $GPa$. According to these results, if pressure is included as an independent variable in the constitutive relations for polyurea in shear under pressure, shear modulus and strength should appear as a piecewise linear function of pressure.

3.3.2 Shear Strain Rate

![Shear stress-strain curves of H2S8(λ = 2) at T=0.55 under low pressures (left) and high pressures (right) at varying strain rate. (units of strain rate: $s^{-1}$). The color legend provided applied to curves with and without markers.](image)

Shear strain rate is another critical parameter when we study dynamics of polymers below $T_g$ since polymers in the rubbery state display frequency-dependent behavior. However, the polyurea studied in this dissertation includes high-$T_g$ hard domains and is in the so-called “leathery state” at room temperature (T=0.55). Applying high-level pressures can increase the overall $T_g$ of the whole copolymer, resulting in low sensitivity to slight changes in strain rate. This effect helps to decouple the effect of strain rate from the pressure effect in the PSPI experiments [27-30], where
the shear strain rates applied are between $10^5$ and $10^6 \text{s}^{-1}$. To provide evidence for the low sensitivity within this strain rate range at various pressure levels, we simulate cases with strain rate variations at several pressures. Every set of shear stress strain curves at the same pressure level from 0.6 to 8.1 $GPa$ in Figure 20 show slight differences when variation of shear strain rate is within one to two decades. More importantly, the glass transition temperature of polyurea is reported to reach room temperature when pressure is around 1 $GPa[141]$. Therefore, in most cases in Figure 18 and Figure 20, polyurea is in a glassy state. Overall, the results (Figure 20) indicate that the strain rate effect can be neglected safely relative to the influence of pressure in the PSPI experiments[27-30]. As for the influence of strain rate in a much larger scale, the viscoelastic performance of this copolymer in a frequency range larger than two decades will be presented later in the dissertation.

3.3.3 Temperature

![Figure 21 Shear stress-strain curves of H2S8($\dot{\gamma} = 2$, shear strain rate of $1 \times 10^6 \text{ s}^{-1}$) at two pressure](image)
conditions, showing the effects of temperature on shear resistance with $T=0.3$, $T=0.55$ and $T=1.0$ (In reduced units, $T=0.55$ corresponds to room temperature for PU1000). The color legend provided applies to curves with and without markers.

At relaxed state, the $T_g$ of soft domains remains around $-60^\circ C$ [49] (about 0.39 in reduced temperature units), whereas the $T_g$ of hard domains changes with the fraction of hard segments and interaction between hard beads. To examine the effect of temperature and how this effect changes with the applied pressure, shear deformation simulations are carried out with PU1000 at three different temperatures at two pressure levels. For all cases in Figure 21, $T=1.0$ is a very high temperature, at which both the soft and hard domains are in their rubbery states. $T=0.55$ corresponds to room temperature and lies in between the $T_g$ of the soft and hard domains. We also include a very low temperature $T=0.3$, which is below $T_g$ of both the soft and hard domains. Note that the magnitude of the temperature effect changes for different pressure loadings. For instance, among low pressure cases ($0.8 GPa$ in Figure 21), the copolymer acts like a liquid at $T=1.0$ and behaves more solid-like at $T=0.55$ and $T=0.3$. The results indicate that hard domains with $T_g$ higher than the simulation temperature significantly increase the overall stiffness and strength. In contrast, when the pressure increases to $2.4 GPa$ (Figure 21), the copolymer is so compact and interaction between segments becomes so strong that it exhibits high stiffness even at a high temperature like $T=1.0$. This densification effect is consistent with the experimental results[141], which provide an explanation for the above response. When pressure is $2.4 GPa$, the $T_g$ of the whole copolymer becomes higher than $T=1.0$ so the material is in a glassy state although both of its phases are in rubbery state when no pressure is applied. This also explains why the differences in shear response between the three temperatures are reduced: they are all in
a glassy state at the high pressure (2.4 GPa).

3.3.4 Volume Fraction of Hard Domains and Energy Factor between Hard Beads

![Shear stress-strain curves for each PU formulation under varying pressure conditions at (a) \( \lambda = 2 \); (b) \( \lambda = 5 \), showing the effect of hard bead fraction on shear resistance.](image)

In addition to simulating the response of PU1000 (H2S8) which is a very commonly used polyurea formulation in applications, we also conduct simulations on another two polyurea structures PU650 (H2S5) and PU250 (H2S2) in order to explore the impact of hard bead fraction on shearing resistance under various pressure levels. The shear strength for the three copolymers is similar for each pressure level when the hard-hard interaction is small (\( \lambda = 2 \) in Figure 22-a). As discussed in Section 3.1, hard segments with small \( \lambda \) are not able to form domains with large stiffness. As a result, the strengthening effect from a high fraction of hard segments is weak and the shear strength of H2S2 is only slightly higher than that of H2S5 or H2S8. More importantly, the initial shear moduli and shear strength become closer at a high-pressure level due to densification since high pressure dominates the shear resistance. Conversely, the results for simulations with \( \lambda = 5 \) are significantly different. This is because strong hard-hard interactions
lead to stiffer hard domains. Consequently, increasing the fraction of hard segments can greatly stiffen the overall copolymer. Note that the difference between responses of H2S8, H2S5 and H2S2 with $\lambda = 5$ at low pressure are larger than those with $\lambda = 2$. Additionally, when pressure increases to a high level, the stiffness imparted by increased fraction of hard beads is significantly larger for $\lambda = 5$ compared to $\lambda = 2$. For example, the plateau stress increases by only 13% for the $\lambda = 2$ case at the pressure of 1.6 GPa between H2S8 and H2S2 but increases by 59% for the $\lambda = 5$ case.

3.4 Conclusion

Using the generic bead-spring CGMD model, morphologies of hard-soft copolymer systems with different composition and interaction between hard beads indicate the interaction dominates phase separation of hard and soft domains. As for the shear resistance under, we found that among all the factors investigated (applied pressure, shear strain rate, temperature, fraction of hard segments and interaction between hard beads), pressure is the most critical one because compression causes material densification, which increases stiffness. Moreover, when including pressure as a parameter in shear constitutive relations, both the initial shear moduli and shear strength are a piecewise linear function of pressure. In addition, the coupled effects of hard phase fraction and interaction between hard segments, together with temperature, also show considerable influence on the shear performance by contributing to the crystallization of hard domains.
Chapter 4  Property Calculation for Soft and Hard Phases using CGMD models

In this chapter, the calculation of mechanical properties for each phase is presented based on the CGMD model in Chapter 3, including viscoelasticity of the soft matrix and elastic constants of the hard domains, respectively. For viscoelastic calculations in the current work, we employ the stress auto correlation function [51] to compute the stress relaxation, which is fitted in Prony series using a two-step optimization method. We increase the run time up to \(10^7 \sim 10^8\) steps and provide sufficiently accurate estimates of the linear rheological properties of hard-soft copolymer melts. For local modulus calculation, we first show how to calculate effective local strain of hard domains using the method presented by Falk and Langer[89] and validated in a series of papers by de Pablo et al[90-92]. Together with local stress tensors, local elastic constants can thus be computed using a fully local stress strain fluctuation method. Finally, we summarize this chapter and state how the results from this chapter can be used in further research.

4.1 Viscoelastic Properties of Soft Matrix and the Hard-Soft Copolymers

Understanding of the mechanism responsible for the excellent energy dissipation properties of polyurea is still unclear. A plausible source of the dissipative properties of polyurea is its multiblock architecture composed of repeating units of hard and soft segments. In this section, we use the simple model of polyurea described above which provides an excellent platform for the following analysis to examine if and how the polyurea’s architecture endows it with superior energy dissipation, and more generally how variations in the structure, composition, and interactions of polyurea affect its properties at a qualitative level.
The viscoelastic properties of copolymers are computed using equilibrium MD simulations performed in the canonical (NVT) ensemble. The simulation temperatures are set to be $T = 1.0$ and $T = 0.55$ using a Nose-Hoover thermostat[128], with the latter corresponding to room temperature. A standard velocity-Verlet algorithm is used to integrate the equations of motion with a time step of $\Delta t = 0.005\tau$, the same with previous studies. The preparation of the simulation box has been explained in Chapter 2. All the simulations are run for $1 \times 10^8$ time steps, and the time-dependent shear modulus is computed from the stress autocorrelation function (SACF) [20, 51, 58, 62]

$$G(t) = \frac{V}{k_B T} \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle$$

(12)

denotes ensemble average. Stresses here are the shear stress part from,

$$\sigma_{xy} = \frac{1}{V} \left[ \sum_{\alpha} m_{\alpha} (v_{\alpha})_x (v_{\alpha})_y - \sum_{\beta > \alpha} \frac{\partial U_{\alpha \beta}}{\partial r_{\alpha \beta}} (r_{\alpha \beta})_x (r_{\alpha \beta})_y - \sum_{\beta > \alpha} \frac{\partial U_{\alpha \beta}}{\partial r_{\alpha \beta}} (r_{\alpha \beta})_x (r_{\alpha \beta})_y \right]$$

(13)

and the Newtonian shear viscosity, $\eta$, can be computed using the Green-Kubo formulation

$$\eta = \int_0^\infty G(t) \, dt$$

(14)

where $V$ is the system volume, $r_{\alpha \beta}$ is the distance between $\alpha$ th and $\beta$ th beads, and $m_{\alpha}$ and $v_{\alpha}$ are the mass and velocity of $\alpha$ th bead. The first term specifies the kinetic energy contribution, and the second term specifies the bonded and nonbonded energy contributions. Since the three off-diagonal elements of the stress tensor $\sigma_{xy}$, $\sigma_{yx}$ and $\sigma_{zx}$ are equivalent for isotropic systems, we
use the average of the three stresses to get a smoother estimate of the stress relaxation. Note that the stresses need to be computed and outputted at each time step to obtain accurate results, as in previous studies [20, 51]. With the stress tensors outputted at each time step for total $10^7 \sim 10^8$ steps using LAMMPS [127], Eqn. (12) is applied and the dynamic shear modulus is calculated for each case.

The dynamic shear moduli of the hard-soft copolymers in several conditions are plotted in Figure 23. This behavior can be represented generally in three stages. At short times from $t = 0$ to $t = 0.1$, the dominating mechanism for stress relaxation is the rearrangement of bond lengths and is independent of the microstructure. Hence, the $G(t)$ values for the five systems are similar at short times. At intermediate times, stress relaxation is the result of the reorientation of polymer chain segments, and the evolution of $G(t)$ begins to diverge for the different cases. For example, Rouse behavior can be observed for a polymer above its $T_g$, whereas a plateau might occur for hard-soft copolymers with large hard-hard interactions due to the immobilization of hard segments. At long times, $G(t)$ falls rapidly, indicating that our simulations are long enough to capture the entire stress relaxation process. To reduce the noise in $G(t)$ at long times, we calculate the average value of $G(t)$ from $0.9t$ to $1.1t$ for each time $t$ as in previous studies[20, 58].

While all of the copolymer simulations displayed these three distinct stages, Figure 23 provides more information regarding how composition affects the intermediate-time regime. At temperature $T = 0.55$, the soft domains of the matrix are in the rubbery state and thus display Rouse-behavior relaxation, whereas the copolymers show less relaxation than the soft matrix due to the presence
of the hard domains. The three copolymers with $\lambda = 2$ gradually display more “solid-like” behavior with increasing fraction of hard beads since the degree of vitrification of hard domains increases accordingly. For a given soft-hard ratio, a larger energy factor slows stress relaxation and results in a higher dynamic shear modulus (e.g., H2S8- $\lambda = 5$ vs. H2S8- $\lambda = 2$). Thus, increasing either the fraction of hard beads or the interaction between hard beads can lead to a larger degree of vitrification and retard the stress relaxation. In particular, for H2S2- $\lambda = 2$, stress relaxation becomes weak and a plateau is observed due to the high fraction of hard beads and the extremely low mobility of hard segments. Similar but more prominent plateaus were observed in the time-dependent shear modulus, $G(t)$, of the polymer nanocomposites [142-144] due to the reduced mobility of polymer segments near particle surfaces. The observations from the current simulation results indicate that the response of the block copolymers is intermediate to that of homo-polymer melts (pure soft material in our simulations) and polymer nanocomposites.
Figure 23 Time-dependent shear moduli, $G(t)$, for hard-soft copolymers, showing (a) the effect of composition and interaction between hard segments ($\lambda$) and (b) the effect of temperature for cases of the soft phase and H2S8 with two energy factors. The inset shows the short-time behavior for both (a) and (b).

In addition to microstructural features, temperature is another dominant parameter for stress relaxation. All dynamic shear moduli at $T = 1.0$ decrease relative to their counterparts at a lower temperature $T = 0.55$. It should be noted that H2S8- $\lambda = 2$ at $T = 1.0$ also exhibits the Rouse
behavior of the soft matrix, indicating that $T = 1.0$ is above $T_g$ of its hard domains and both phases become rubbery. The same behavior is not observed for H2S8- $\lambda = 5$ despite sharing the same composition because the stronger interaction between hard beads leads to a higher $T_g$ of hard domains, higher than $T = 1.0$. As a consequence, the copolymer retains more “solid-like” behavior and the stress relaxation slows down.

![Figure 24 Viscosity in reduced units at various compositions. The trend for $\lambda = 2$ with increasing hard segment fraction is indicated by solid lines with solid circles, and the trend for PU1000(H2S8) with increasing energy factor is indicated by dashed lines with open triangles. The compositions are the same as those in Figure 15, and lines are drawn as visual aides. The Newtonian shear viscosities calculated with Eq. (14) are given in Figure 24. As expected, a higher fraction of hard segments leads to increased viscosity. This strengthening effect is magnified at $T=0.55$, where the temperature is below $T_g$ of the hard domains. Moreover, a higher energy factor also increases viscosity because larger attractive forces precipitate the vitrification process in hard domains and restrain their movements.](image-url)
To take advantage of the MD results in future FE modeling efforts – that is, to provide the necessary viscoelastic constitutive relations for polyurea in a format convenient to support future continuum computational studies – the dynamic shear modulus is converted into frequency-dependent complex form:

\[ G^* (\omega) = i\omega \int_0^\infty e^{-i\omega t} G_{xy}(t) dt. \]  

The storage modulus and the loss modulus can be computed by:

\[
\begin{align*}
G'(\omega) &= \omega \int_0^\infty G_{xy}(t) \sin(\omega t) dt, \\
G''(\omega) &= \omega \int_0^\infty G_{xy}(t) \cos(\omega t) dt,
\end{align*}
\]

respectively. Another way to represent the dynamic shear modulus is through Prony series expansion:

\[ G(t) = G_0 \left( 1 - \sum_{i=1}^N G_i \left( 1 - e^{-t/\tau_i} \right) \right), \]  

where \( G_i \) and \( \tau_i \) are material parameters and \( G_0 \) is the instantaneous modulus. With coefficients determined by fitting \( G(t) \) through Prony series expansion, the corresponding \( G'(\omega) \) and \( G''(\omega) \) are given as follows:

\[
\begin{align*}
G'(\omega) &= G_0 \left( 1 - \sum_{i=1}^N G_i \right) + \sum_{i=1}^N \frac{G_i \tau_i^2 \omega^2}{1 + \tau_i^2 \omega^2}, \\
G''(\omega) &= \sum_{i=1}^N \frac{G_i \tau_i \omega}{1 + \tau_i^2 \omega^2},
\end{align*}
\]
To determine the coefficients of the Prony series expansion in (17) for a viscoelastic constitutive model, we employ a two-step optimization process. The particle swarm optimization method is used for instantaneous modulus, $G_0$, and relaxation times, $\tau_i$, while a linear least squares solver is used for $G_i$. Detailed description of this method are discussed in Chapter 2 and can also be found in Ref. [67].

![Dynamic Shear Modulus vs Time (in reduced units)](image1.png)

![Dynamic Shear Modulus vs Time (in reduced units)](image2.png)

![Dynamic Shear Modulus vs Time (in reduced units)](image3.png)

![Dynamic Shear Modulus vs Time (in reduced units)](image4.png)

Figure 25 Examples of the fitting results. Starred points are from the MD simulation results, while the lines portray the Prony series fit.
Figure 25 shows fitting results for four copolymer cases in Figure 23-a. Once the fitting accuracy is within expectations, we insert Prony series parameters into Eqn. (18) and obtain storage and loss moduli in frequency domain for each case.

Figure 26 shows the viscoelastic behavior of H2S8-$\lambda = 2$ at $T = 0.55$ in the frequency domain. The general shapes of the curves, like those of most polymers, have dissipation dominating at low frequencies, an elastic region at high frequencies, and a transition region in between. H2S8-$\lambda = 2$ exhibits flow behavior at low frequencies with $G'(\omega) \propto \omega^2$ and $G''(\omega) \propto \omega^1$ (Newtonian fluid behavior). This flow behavior at low frequencies corresponds to the long-term rapid stress relaxation observed in Figure 23-a. Similarly, all materials show the same qualitative behavior at low frequencies in Figure 27 since the soft domains of the copolymers exhibit flow behavior at sufficiently low frequencies.
Figure 26 Storage and loss modulus of H2S8- $\lambda = 2$ after transferring the time-dependent shear modulus to the frequency domain. The inset shows the loss tangent in the same frequency range.

Like the dynamic modulus curves for H2S8- $\lambda = 2$, all copolymers display behavior with three distinct regimes along the frequency range, yet differences between the curves arise due to changes in composition or hard-hard interactions (Figure 27 and Figure 28).

First, both storage $G'(\omega)$ and loss $G''(\omega)$ moduli of different copolymers tend to converge at very high frequencies. As is the case for very short times in stress relaxation (Figure 23), this is due to the correlation between microstructures and the dominance of relaxation processes of individual bonds at high frequencies.

Second, all copolymers finally yield flow behavior at low frequencies since the soft matrix dominates their viscoelastic performance in the low frequency range. However, the frequencies at which storage $G'(\omega)$ and loss $G''(\omega)$ moduli begin to drop differ for the different copolymers. For example, copolymers with increased degree of vitrification in the hard domains (i.e. H2S2- $\lambda = 2$ and H2S8- $\lambda = 5$) display liquid-like behavior at much lower frequencies than those with less degree of vitrification or reduced fraction of hard segments.

Finally, the strengthening effects of hard beads and large $\lambda$ are consistent across the entire frequency range but not across different temperatures. For example, H2S2- $\lambda = 2$ is stiffer than H2S8- $\lambda = 5$ at $T = 0.55$ (Figure 27-a) in the full frequency range while the opposite occurs at $T = 1.0$ (Figure 28-a). Although the fraction of hard beads and the interaction between hard segments both can stiffen the copolymer, and these effects can be coupled, this is not the case at all temperatures, due to the role of energy factor in determining $T_g$ of the hard domains. The
strengthening effect due to hard phase fraction weakens at high temperatures approaching $T_g$ of the hard domains in H2S2. In contrast, the storage modulus of H2S8- $\lambda = 5$ only decreases a minor level relative to H2S2 because $T = 1.0$ is still far below $T_g$ of the hard domains. Understanding of this principle is essential for designing copolymers for use at a given working temperature or in applications where the temperature is expected to fluctuate.

![Figure 27](image1.png)

**Figure 27** Frequency-domain storage modulus (a), loss modulus (b) and $\tan \delta$ (c) for hard-soft copolymers with different hard-segment fraction and energy factors at $T = 0.55$.

![Figure 28](image2.png)

**Figure 28** Frequency-domain storage modulus (a), loss modulus (b) and $\tan \delta$ (c) for hard-soft copolymers at $T = 1.0$.

### 4.2 Local Modulus of Hard Domains

Unlike the soft matrix, which is in the rubbery state at room temperature, the rod-shaped hard domains are in their glassy state due to their high $T_g$ (above room temperature). Hence, we
calculate their local elastic constants depending on the fluctuation techniques in the NPT ensemble, implemented by a Nose-Hoover thermostat[128] and a Parrinello-Rahman pressostat. The external pressure is fixed as 0. The velocity-Verlet algorithm is chosen to integrate the equations of motion. All the simulation systems are first equilibrated in the NPT ensemble and then evolved to collect the results. The stress-strain fluctuation formula can be expressed as follows:

\[ C_{ijkl} = \langle \sigma_{ij} \epsilon_{mn} \rangle \langle \epsilon_{mn} \epsilon_{kl} \rangle^{-1}, \]  

(19)

where stress \( \sigma_{ij} \) and strain \( \epsilon_{mn} \) tensors are defined within the domain to be considered. To give an example of how to realize the stress and strain method, we first show the results of elastic constants with global stress and strain. The corresponding global stress tensor with our potential in CGMD model is

\[ \sigma_{ij} = \frac{1}{V} \left[ \sum_{\alpha} m_{\alpha} (v_{\alpha})_{i} (v_{\alpha})_{j} - \sum_{\beta > \alpha} \frac{\partial U_{\text{FENE}}}{\partial r_{\alpha \beta}} (r_{\alpha \beta})_{i} (r_{\alpha \beta})_{j} - \sum_{\beta > \alpha} \frac{\partial U_{\text{LJ}}}{\partial r_{\alpha \beta}} (r_{\alpha \beta})_{i} (r_{\alpha \beta})_{j} \right] \]  

(20)

where \( V \) is the volume of system and \( r_{\alpha \beta} \) is the distance between \( \alpha \) th and \( \beta \) th beads. \( m_{\alpha} \) and \( v_{\alpha} \) are the mass and velocity of \( \alpha \) th bead.

Before proceeding to the calculation results, we need to point out the linear elastic assumption of the fluctuation method, which requires both strains and strain fluctuations to be sufficiently small. It is well known that a polymer becomes very soft when transiting into the rubbery phase above \( T_{g} \). However, it is difficult to obtain accurate mechanical properties at this temperature since the strains could be very large, although the polymer is still in the solid state. Shown in
Figure 29(a) are the six engineering strains at a temperature of 0.55, which are as large as 10%.
Clearly, such large strain behavior breaks the linear assumption and necessitates some alternative methods. One solution is to use the elastic bath method [82, 84] to ensure a system within linear elasticity. The concept of this technique is to immerse the simulation system into an elastic bath with appropriately chosen modulus, where both stresses and strains can be amplified or attenuated. Since the elastic bath is merely a mathematical construction, the elastic constants can be chosen freely, including nonphysical values, i.e., less than zero, which can be used to amplify fluctuations. According to the recent work [84], Eqn.(19) can be applied for the calculation of modulus with elastic bath. For simplicity, an isotropic material is employed as the elastic bath, and the elastic constants are given by

\[
C_{11} = \lambda + 2\mu, \quad C_{12} = \lambda, \quad C_{44} = \mu
\]  

(21)

where, \( \lambda \) and \( \mu \) are the Lame coefficients. These parameters are set as 10 after several preliminary calculations, guaranteeing that all the strains are less than 5% (e.g., Figure 29 (b)). Under these conditions, all the moduli show fast convergences. An illustration of all soft-bead material at temperature of 0.55 (above \( T_g \), see later) is depicted in Figure 30. With this method, we recalculate the physical properties. The results are performed in the following subsections.
Figure 29 Six engineering stain evolution a) without b) with elastic bath method.

Figure 30 Convergence of elastic constants of $C_{11}$, $C_{12}$ and $C_{44}$.

Based on the stress-strain fluctuation formula, we compute the bulk and elastic moduli directly. The results are depicted in Figure 31. These moduli increase by including hard segments, especially for higher energy factor and volume fraction. Young’s modulus changes at least one order of magnitude before and after $T_g$ from Figure 31 (b). In addition, the materials with small $\lambda$ (H2S8-2 and H2S3-2) show similar behaviors above $T_g$ due to their ‘liquid-like’ structures of both
hard and soft domains.

Figure 31 (a) Bulk and (b) shear moduli as a function of temperature for hard/soft materials.

As discussed in Chapter 2, to calculate local elastic constants using Eqn. (19), we need to define local stress and local strain tensors for the hard domains. Without loss of generality, every bead is recognized as one single domain, indicating that these local variables represent the average effects over all the hard beads in the local region. Thus, the required local variables become per-bead stress and per-bead strain tensors. Based on the assumption of equal contributions from each bead, the per-bead stress can be defined as [145]:

\[
(\sigma_{ij})_\alpha = \frac{1}{V_\alpha} \left[ k_B T \delta_{ij} + \sum_m k_m (r_m)_\alpha (f_m)_\alpha \right],
\]

where \(V_\alpha\) is the average bead volume, \(k_B\) is the Boltzmann constant, \(T\) is the temperature, and \(k_m\) is the weighting factor, which is equal to 1/2 for pairwise non-bonded potential and bonded potential, 1/3 for angle potential, 1/4 for dihedral potential, and so forth. Since it is a symmetric tensor for each bead, only six independent components are stored. The per-bead volume \(V_\alpha\) is not
readily defined or measured, especially in the deformed state. In our work, we use a Voronoi tessellation to approximate $V_\alpha$. Note that the global stress can be recovered by averaging the stress of each bead from Eqn. (22).

![Stress plots](image)

Figure 32 Stress levels of (a) soft matrix and hard domains: (b) $\lambda = 2$, (c) $\lambda = 3$, (d) $\lambda = 5$.

To compare with the stress levels in hard domains for different energy factor cases (Figure 32), we also show the corresponding global stress levels
For the per-bead strain, since it doesn’t work to represent local strain tensor with global strain tensor in hard-soft block copolymer systems, we use the method introduced by Falk and Langer [89] to compute the closest possible approximation to a local strain tensor in the neighborhood of a hard bead. As shown in Figure 34, an interaction range is first defined by considering the neighboring beads that lie within a domain of radius $2.5\sigma$. Within this interaction range, the first part in Eqn. (23) $r'(t) - r_0'(t)$ is the actual displacement of green neighboring beads relative to the red ones and the second part is the relative displacements they would have if all green beads were in a region with a uniform strain $\varepsilon_{ij}$. The local strain $\varepsilon_{ij}$ is defined to minimize the mean square difference $D^2(t, \Delta t)$ between the actual displacements of the neighboring beads and the relative displacement – that is, to minimize the nonaffine part of local displacements.
The mean-square difference is defined as:

\[
D^2(t, \Delta t) = \sum_n \sum_i \left( r^i_n(t) - r^i_0(t) - \sum_j (\delta_{ij} + \varepsilon_{ij}) \left[ r^j_n(t - \Delta t) - r^j_0(t - \Delta t) \right] \right)^2
\]  

(23)

where the indices \(i\) and \(j\) denote spatial coordinates and the index \(n\) runs over the beads within the interaction range of the reference bead, with \(n = 0\) being the reference bead. \(r^i_n(t)\) is the \(i\)th component of the position of the \(n\)th bead at time \(t\). We then calculate \(\varepsilon_{ij}\) through Eqn. (25) with calculating \(X_{ij}\) and \(Y_{ij}\) in Eqn. (24).

\[
\begin{align*}
X_{ij} & = \sum_n \left[ r^i_n(t) - r^i_0(t) \right] \left[ r^j_n(t - \Delta t) - r^j_0(t - \Delta t) \right] \\
Y_{ij} & = \sum_n \left[ r^i_n(t - \Delta t) - r^i_0(t - \Delta t) \right] \left[ r^j_n(t - \Delta t) - r^j_0(t - \Delta t) \right] \\
\varepsilon_{ij} & = \sum_k X_{ik} Y_{jk}^{-1} - \delta_{ij}
\end{align*}
\]

(24)

The minimum value of \(D^2(t, \Delta t)\) is the local deviation from affine deformation during the time

Figure 34 Schematic representation of the interaction range defined for local strain of the red bead.
The per-bead stress and per-bead strain obtained from the above methods are averaged for all the hard beads in the whole simulation box. With those inserted in Eqn. (19), results of the elastic constants of hard domains are shown in Figure 35. Different fraction and interaction of hard segments are considered.

![Graphs showing Young’s moduli and shear moduli](image)

Figure 35 (a) Young’s moduli and (b) shear moduli of local hard domains in copolymers with different combination of hard-segment fraction and energy factor.

For each material composition, hard domains become stiffer with larger energy factor. This indicates that higher binding forces within hard domains makes them more compact and stiffer, which gives a larger elastic constant. Conversely, each curve in Figure 35 shows that both Young’s and shear moduli of local hard domains increase when the material includes more hard segments at a fixed energy factor. This trend is more drastic for the high-$\lambda$ case (red curves). The modulus increment when increasing hard bead fraction comes from the extra constraints brought by more hard beads in the simulation box. The constraints make it more difficult for all hard beads to move locally and thus decrease the local strain level. Specifically, when volume fraction of hard beads
is larger, more hard beads are included in the interaction range to calculate the per-bead strain, which leads to a lower level of the per-bead strain. We also applied the same method to calculate the local elastic modulus of soft domains (designated by the black squares in Figure 35), with two orders of magnitude reduction in modulus relative to those of the hard domains. Since the viscoelastic soft domains are in their rubbery state at this temperature, these values reflect their long-term moduli and are expected to be extremely low.

The results are important for two reasons. First, the methodology can be applied generally to polymer systems and it provides a way to quantitatively measure the mechanical properties of local domains, enabling characterization of the relative influence of molecular-level parameters such as bonded potentials and bead ratios. This is a critical tool because the nanoscale dimensions of each phase and the leathery behavior of polyurea create significant experimental challenges for investigating the performance of two distinct phases in two-phase systems. Second, the results can serve as material inputs for subsequent continuum level analyses such as finite element analysis in more complex systems such as polymer-substrate configurations or polymer composites and nanocomposites. Although MD models can capture essential molecular-scale features, it is still intractable to model macroscale structures and to explore the damage-mitigating effect of polyurea coatings through MD simulations. Due to the lack of detailed investigations in the properties of each phase in polyurea coatings, they are often treated as one single phase with either viscoelastic or plastic-damage constitutive relations in most current continuum models [8, 9, 96]. With the results in this chapter, better constitutive relations can be developed for polyurea films.
4.3 Conclusion

After the morphology study and shear under pressure tests in Chapter 3, we continue the study with CGMD models in this chapter. First, the viscoelasticity of hard-soft copolymers is computed using a stress autocorrelation technique to understand the dynamic response of elastomers and how they mitigate damage in impact loading applications. Dynamic shear modulus $G(t)$ is obtained and fitted with Prony series using a two-step optimization method. From $G(t)$ of copolymers with different compositions, pure rubbery behavior is observed for the soft matrix, whereas the response becomes more solid-like with the addition of more hard segments. Furthermore, storage and loss modulus curves in frequency domain are presented by transferring $G(t)$ into $G'(\omega)$ and $G''(\omega)$ with Prony series parameters. Second, local elastic constants of hard domains are computed by replacing global variables with local ones using a general stress-strain fluctuation algorithm. Definition of local strain of a single bead is introduced and the local strain of a hard domain is the averaging effect of all hard beads in that domain. With that, the local elastic constants of hard domains are calculated with purely local stress and local strain tensors. Again, the coupled effect of hard phase fraction and interaction between hard segments dominates their elastic moduli. The obtained mechanical properties of each phase can be used as the inputs for continuum models for two-phase systems. Since the results are directly related to molecular features, they can provide new insights that will enable the tailoring of the microstructure of TPUs to optimize their performance in penetration and fragmentation resistance of metallic/polymer systems and to provide better understanding that reflects the influence of microstructure and composition on macroscopic properties.
Chapter 5  Study on Effect of Interphase using FEA Pixelated Model

In this chapter, a finite element framework is built up to simulate linear viscoelastic response of hard-soft block copolymers by introducing gradient interphase layers between hard and soft phases. We first employed Ni-black image processing method to binarize the preprocessed AFM image and then imported the binary digitized image into ABAQUS as the geometry input. Interphase layers are added in this process. Material properties of each phase are obtained from a combination of both MD simulations and DMA calibration of the polyurea. The response is obtained after simulations are done on structures with varying degrees of interphase occupation and its property distribution across the occupation. Qualitative analysis on impact of interphase properties is then presented. Following that, a ranking algorithm is run by representing the interphase layers with a 15-element vector and extracting features of the vector to describe interphase features. The importance of each interphase feature in determining the responses is given quantitatively. The 2D approach is a simplified realization of the 3D model with less requirement for computational cost, the trends in the results are generalizable to other 3D configurations. To show the reliability of this generality of using 2D models, we also include 3D reconstructed microstructures and results are shown at the end of this chapter.

5.1  Image Processing Technique

Microstructures of polyurea consist of phase separated hard domains and soft matrix. With the original AFM phase image [140] in Figure 36-(1), one can visually identify the rod-shaped hard domains, however, deliberate image processing is required to quantitatively represent the hard domains in a way that is usable in numerical simulations. Therefore, an image binarization
algorithm is performed on the AFM phase image while maintaining proper volume fraction of hard domains. To increase the binarization accuracy and remove the 3D effect in the AFM image, the brightness and contrast of the original AFM phase image is first increased as in Figure 36-(2).

![Figure 36](image-url)  
Figure 36 Image preprocessing and binarization, (1) original AFM image comes from the reference[140]†, (2) brightness increases, (3) image with two phases after binarization, (4) small dots are removed.

In the image binarization algorithm, binarization is applied to identify the gray-scale pixels as either hard domains or the soft matrix. Global threshold-based techniques are typically used which were originally proposed for recognizing texture from a gray-scale document page. In these techniques, a global threshold, $T$, determined by statistical criteria, is used as the decision boundary for the binary classification problem [146, 147]. Small portions of misclassification or noise does not influence the identification results for document pages while it can cause lots of problems in application for our AFM phase images. For example, small areas of uneven background brightness, especially shadows created by voids, wrinkles or uneven thickness can be

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misclassified as an incorrect phase and change the morphology of hard domains, and further result in significant error. To address this problem, instead of using a global threshold method, local threshold algorithms based on a sliding window were employed. Several pixel-wise threshold algorithms [148] have been evaluated on the TEM images of our polymer nanocomposites with both small volume fraction (around 1%) and small areas of uneven brightness. The Niblack algorithm [149] was found to perform the best among these algorithms. In the Niblack algorithm, the pixel-wise threshold is computed as follows:

$$T_{\text{Niblack}} = m + k \sqrt{\frac{\sum p_i^2}{N_p}} - m^2$$

(26)

where $m$ is the local gray-scale mean of the pixel’s neighbor area, $i$ enumerates all the pixels in the neighbor area (in the sliding window), $p_i$ is the gray-scale value of pixels, and $N_p$ is the total number of the pixels in the neighbor area chosen based on the area of uneven brightness ($k$ is an empirical constant that is set to $-0.2$ by the authors [148, 149]). Details of the comparison between using the global threshold-based techniques and the Niblack algorithm were presented in Ref [150] and it’s indicated that Niblack algorithm is a more accurate binarization algorithm to process phase images and the resulted gray-scale image is well binarized with minimal undesired misidentifications. The final microstructure with soft matrix, interphase layers (introduced in Section 3) and hard domains, is in the format of a 0-1 matrix, which is suitable for mapped mesh (one pixel is one element).

To prepare for the quantitative analysis of significance ranking of interphase features like thickness and property, a large amount of data is needed, and one two-phase microstructure from
experiments is not enough to generate the required amount of data. To take one step further in the stage of image processing and microstructure preparation, we employ a generalized transfer learning-based, training-free approach [151] to reconstruct statistically equivalent microstructures from the original binarized AFM image (Figure 36-(4)). The approach incorporates an encoder-decoder process and feature-matching optimization using a deep convolutional network. The input microstructure with labeled material phases is first passed through an encoding process to obtain a 3-channel representation and the initial 3-channel representation is randomly generated as the initialization. In each iteration of the reconstruction process, the 3-channel representations of both the original and reconstructed microstructures are fed into a pre-trained deep convolutional network, and a loss function is utilized to measure the statistical difference between them. A specific optimization technique is used to update the reconstructed microstructure. Finally, the updated 3-channel representation of the reconstructed microstructure is propagated through a decoding stage via unsupervised learning to obtain the reconstructed microstructure with labeled material phases. Details of the reconstruction process can be found in the Ref [151]. Ten statistically equivalent two-phase microstructures are reconstructed, and response data are collected after running FEA simulations. With these data, quantitative interphase feature significance ranking is presented in 5.4.

5.2 Pixelated FEA Techniques for Interphase Study

A plane strain finite element model is employed to calculate the viscoelastic response of hard-soft copolymers with different interphase scenarios in this paper. Besides utilizing the discretization of 2D binarized AFM image as the geometry inputs, we present how the material
inputs for all three phases are obtained as follows.

1. Viscoelastic property of soft matrix

One way to shape polymers’ damping property in the frequency domain is the \( \tan \delta \) curves, \( \tan \delta = \frac{G''}{G'} \), where \( G'' \) is the shear loss modulus and \( G' \) is the shear storage modulus. \( \tan \delta, G' \) and \( G'' \) are all functions of frequency \( \omega \). The viscoelastic property of polymers means that when applying a sinusoidal load (stress) to the structure and measuring the resulting displacement (strain), a phase lag between stress and the resulting strain will be observed in materials with viscosity. For example, \( \delta = 0^\circ \) for a perfectly elastic solid (stress and strain are perfectly in phase); \( \delta = 90^\circ \) for a purely viscous fluid. Viscoelastic materials will show a phase lag \( \delta \) between \( 0^\circ \) and \( 90^\circ \). The elastic portion of viscoelastic materials is represented by the shear storage modulus that measures the stored energy and the viscous portion is measured by the shear loss modulus that measures the energy dissipated as heat.

To obtain the dynamic modulus of the polyurea systems, Amirkhizi et al. [48, 49] conducted DMA tests on a polyurea system (PU1000) and developed master curves of storage and loss modulus using time–temperature superposition principle. The curves lie mostly in the leathery state (\( < 10^{11} \ Hz \)). To borrow this data of PU1000 and construct that of the soft matrix to cover the full transition regime, we first calculate the storage \( (G') \) and loss \( (G'') \) modulus of the soft matrix using molecular dynamics in high frequency range [152] (\( > 10^9 \ Hz \)). Then we calculate \( E', E'' \) and \( \tan \delta = \frac{E''}{E'} \) from MD data, all of which are functions of temperature and frequency. Here we
assume that the shape of the storage modulus curve for the soft matrix at low frequencies is similar to that of the PU1000 from DMA result (solid black curve in Figure 37). The storage modulus curve of PU1000 is then translated and rotated to match MD results in the overlapped frequency region (Figure 37). After that, we match the \( \tan \delta \) curve in the overlapping frequency range (Figure 37-inset). Consequently, the loss modulus curve is calculated, as shown in Figure 38 (dashed blue curve), together with the storage and \( \tan \delta \) curve. Figure 38 shows the finalized viscoelastic master curves we use for later FEA simulations.

Figure 37 Matching storage modulus and \( \tan \delta \) curves of soft matrix from DMA data at low frequencies and MD data at high frequencies. For the storage modulus, only PU1000 data is available (black curve). To get the soft matrix data, we keep its shape, translate it (green curve) and rotate it (solid blue curve) to match the MD data in the overlapping frequency range. The inset shows the \( \tan \delta \) curve match (blue curve).
2. Elastic constants of hard domains

The $T_g$ of the hard domains in polyurea is over 100°C [16], which is above the simulation temperature (room temperature) in this paper. It’s also noted that this paper focuses on size and property distribution impact of the interphase. Hence, the hard domains are assigned to be linear, elastic, and isotropic for simplicity. The modulus of hard domains is at the same order of magnitude with the instantaneous modulus of soft matrix according to our previous MD estimations [152]. Young’s modulus of hard domains are chosen to be 5 GPa, 15 GPa, and 36 GPa for PU1000 case, where 5 GPa and 36 GPa correspond to $\lambda = 2$ and $\lambda = 5$ cases in our previous coarse-grained MD simulations [152]. Those two values set the lower and upper boundaries of the modulus of hard domains.

3. Dimension and property of interphase domain

The presence of the hard domains alters the physical properties of the neighboring soft polymer chains due to physical and/or chemical interactions at the hard-soft interface, creating an interphase with different properties from the bulk matrix. However, determination of the interphase properties...
is challenging both experimentally and numerically. Experimental methods capable of the necessary resolution to measure those local properties require complex sample preparations and a number of assumptions leading to uncertainties. Numerical calculations such as MD can capture some structural and dynamic details of interphase response, but only at molecular time and length scales which are hard to scale to the continuum level. Fortunately, both computational and experimental work to date can provide guidance on the effects of restricted mobility of polymer chains near stiff nanoparticles [143, 153-156]. Both MD simulations [143, 153-155] and experiments [125, 157] show that $T_g$ of a nanocomposite can be on the order of ten degrees higher than the pure matrix materials, and that the $T_g$ changes in a gradient fashion from the interface [158]. Recent AFM characterization [99, 102] illustrate a gradient in mechanical properties of a polymer near a silica interface. Based on these works, we assume a gradient in properties near the hard domains and that the interphase’s viscoelastic properties are related to those of matrix, they are a simple shift toward the lower frequencies, corresponding to longer relaxation times of areas closer to the hard domains.

Figure 39 provides a schematic representation of creating the gradient interphase layers. The blue pixel in the center represents one hard domain. It is noted that the actual shape of hard domains is much more irregular, which leads to a more complex boundary. In this scheme, two interphase layers with one-pixel thickness in each layer are added in Figure 39-1 while two thicker interphase layers are added in Figure 39-2. Different interphase properties can be assigned to each layer to represent the gradient. The impact of the interphase thickness and property distribution on the viscoelastic response can then be obtained through parametric study of changing the number of
layers and thickness of each layer.

Figure 39 Schematic representation of adding interphase layers with different thickness. The blue pixel is the hard domain, the green ones are first layer of interphase with a larger shifting factor than those in the outer layer (second layer of interphase). Two cases of thickness are shown.

When the interphase property is regarded as related to those of the soft matrix by a simple shift in the frequency domain towards lower frequencies, the gradience is represented by the shifting factor for each interphase layer. For example, the blue and red curves in Figure 40 shows two properties for interphase layers. Apparently, IP1 corresponds to the layer closer to the soft matrix and IP2 is closer to hard domains.
Figure 40 Master curves of interphase property shifted from that of soft matrix. (1) Modulus curves shifting, the inset is the $\tan \delta$ shifting, (2) Zoom-in of the $\tan \delta$ shifting one decade (red curve) and two decades (blue curve).

**FEA model**

With the binarized/reconstructed microstructures (binary digital images as in Figure 41) and material properties from the combination of DMA data and MD simulation estimations, we set up an FEA model with gradient interphase layers to study the structure-property relation and the role of interphase in polyurea’s viscoelastic response. The dimension of the two phase PU1000 structure in Figure 41 is $441 \text{ nm} \times 441 \text{ nm}$, where each pixel is $1 \text{ nm} \times 1 \text{ nm}$ and becomes one element. We consider the structure large enough because it’s orders of magnitude larger than the single hard domains (about 5nm in diameter and 50 nm in length). Periodic boundary conditions are applied to the structure with linear perturbation in the horizontal direction. The frequency-domain analysis is run with a harmonic displacement loading. The loss and storage moduli are assessed for a spectrum of 100 frequencies at a range of $10^{0} \sim 10^{15} \text{ Hz}$.

Figure 41 Schematics of local morphology and extent of interphase zone after adding interphase layers. (1) two layers, (2) three layers.

Before the detailed analysis of the microstructure-response relations, efforts need to be made to
determine what response features are of our interest. Take the two cases in Figure 41 as an example, the interphase region in Figure 41-(1) is divided into two layers with shifting factor to be 2 and 1 while the interphase region in Figure 41-(2) includes three layers with shifting factor 3, 2 and 1. Both interphase region has the same total interphase thickness. The viscoelastic responses of the two cases, together with the soft matrix and the one without interphase are presented in Figure 42: IP Case 1 in Figure 42 is the response for the structure in Figure 41-(1) and IP Case 2 in Figure 42 corresponds to the structure in Figure 41-(2).

Figure 42 Comparison of (1) modulus and (2) tan δ in systems with different interphase scenarios. The legends for dashed curves in (1) are omitted for simplicity. Dashed curves with the same color are the corresponding $E''$.

The viscoelastic responses differ at various extent for the whole frequency range. It’s important to select representative response values while keep the analysis simple and straightforward. Four response variables are selected in this paper to measure how the viscoelastic property at the whole frequency range and stress relaxation property in the transition domain depends on structural
features: the instantaneous modulus at high frequency end and the long-term modulus at low frequency end in the storage modulus curves in Figure 42-(1), and more importantly, $\tan \delta$ peak shifting and its magnitude decrease in the $\tan \delta$ curves in Figure 42-(2). The location of $\tan \delta$ peak is essential because it is a key indicator of stress relaxation property changes due to the inclusion of hard domains and interphase.

5.3 FEA Simulation Results and Analysis

1. Effect of introducing interphase domain

As discussed in Section 5.2, whether to add interphase region around hard domains in the FEA model makes a difference on overall viscoelastic response of hard-soft copolymers. Before detailed analysis on the effect of interphase thickness and property distribution, a comparison between two simple cases (one with interphase and the other without interphase) are used to show the major response at different frequency stages and why we divide it into three frequency ranges. Master curves are in Figure 43 and stress relaxation at different frequency stages are in Figure 44.
Figure 43 Typical master curve changes showing difference between no-IP and with-IP cases. Shifting factors for the With IP case are 2 and 1; The legends for dashed curves in (1) are omitted for simplicity. Dashed curves are $E''$ as with their solid-curve counterparts in the same color.

It is clearly noticed that the overall damping property change (loss $\tan \delta$ curve in Figure 43-(2)) occurs in the transition region from rubbery state to glassy state, which is also indicated by the stress distribution contour in Figure 44. Stress concentrates only on the hard domains (Figure 44-(3)) for no-IP cases even at the frequency very close to where $\tan \delta$ peak occurs, whereas the stress is more homogenized and there appears clear stress gradient from hard domains to soft matrix, which is more physically reasonable. Here is a detailed observation at the three frequency ranges.

Figure 44 Stress distribution at four frequencies for no-IP (top row) and with-IP cases (second row).
Frequencies from left to right are $7.9 \times 10^4, 1.4 \times 10^9, 1.8 \times 10^{11}, 6.3 \times 10^{14}$ Hz respectively. The zoom-in stress distribution at $1.8 \times 10^{11}$ Hz is shown in the bottom row, (9) no-IP case (sub-section in (3)), (10) with-IP case (sub-section in (7)).

**Low frequency range** ($< 1 \times 10^9$ Hz)

This is the frequency range before the transition region. In this stage, the copolymers are in their rubbery state and storage moduli of both cases w/o interphase are two orders of magnitude lower than their counterparts at high frequency range. Both the storage moduli are higher than that of the soft matrix but there is not much difference between the increased values (Figure 43-(1)), which indicates that the increments are mostly due to the addition of hard domains instead of the interphase effect. The stresses at this frequency range are in low level for both cases (Figure 44-(1) and (2)).

**High frequency range** ($> 1 \times 10^{13}$ Hz)

When they reach their glassy state, the hard-soft copolymers lose most of their energy dissipation capability. Compared with long-term modulus at low frequencies, the instantaneous moduli at high frequencies are even closer with each other for two cases w/o interphase (Figure 43-(2)), which indicates that the interphase has little influence on the instantaneous moduli and property of har domains should play a crucial role in this range. According to Figure 44-(4) and (8), the stress distribution for no-IP case at high frequency is more homogeneous than the with-IP case. Although both stress levels are at an elevated level, band-shaped areas around hard domains are still noticeable for with-IP case.

**Mediate frequency range** (transition region)
The mediate frequency range is the transition region where \( \tan \delta \) peak lies and that we care the most when discussing the stress relaxation behavior of a polymer because it tells plenty of information about the material’s energy storage and dissipation property. It is in this frequency range where interphase content plays a key role. The amount of storage modulus increase is much larger due to adding interphase while the shifting of \( \tan \delta \) peak can only be caused by adding interphase layers (Figure 43). The inclusion of hard domains only causes \( \tan \delta \) peak decrease and has nothing to do with \( \tan \delta \) peak shifting. Figure 44-(2) and (3) shows the stress concentration on hard domains for no-IP cases at two mediate frequencies. The stress changes sharply from that to a much lower level in soft matrix. On the other hand, the gradient of stress around hard domains in with-IP case are much smaller than that in no-IP case. The stress distribution in Figure 44-(7) gives a good example of how interphase layers help homogenizing stress distribution and make the FEA model physically more reasonable.

In the following discussion about effect of interphase variation on the viscoelastic response, we focus on the \( \tan \delta \) curves at mediate frequency range in this section and quantitative analysis on the four response values will be given in Section 5.4.

2. Effect of interphase thickness

The dimension of interphase domains has been a topic with long-time interests in previous researches, but no conclusion is reached on what can solely determine it. Since there is no clear definition of the interphase boundary, the size of interphase region is known to be from tens of nano-meters to hundreds of nano-meters for different material systems. For TPUs systems, it’s extremely difficulty to simply get a look at the morphology of separated soft and hard domains in
experiments, therefore, it’s currently impossible to get the property at different location around the hard domain and to measure the interphase size. Fortunately, with computational models, we can vary the interphase thickness and study how it changes the viscoelastic response. Figure 45 shows five cases with gradually thicker interphase layers. To eliminate the effect of property distribution through the thickness, we choose to use 2-layer interphases as an example with the same shifting factor 2 (dash-dotted line in Figure 46) and 1 (dotted line in Figure 46) in all five cases.

Figure 45 Schematic of morphology with five interphase thickness for two layers of Interphase with shifting factor to be 2 and 1.

Figure 46 $\tan \delta$ curve changes due to increasing interphase thickness. All five cases include two interphase layers with shifting factor 2 (IP2) and 1 (IP1). They have the same thickness, which increases
from t1 to t5 for the presented five cases. \( \tan \delta \) peak changes gradually from the soft matrix to the one closest to the hard domains (IP2).

Starting from the No-IP case with only \( \tan \delta \) peak decrease and no shifting at all, the \( \tan \delta \) peak gradually shifted to the left with thicker and thicker interphase. From the way these \( \tan \delta \) curves evolve, three observations are obtained: 1) Inclusion of hard domains will dramatically decrease the \( \tan \delta \) peak because elastic hard domains have no ability to dissipate energy. In addition, adding interphase layers which have \( \tan \delta \) peak at other frequencies (IP1 and IP2 in Figure 46) will further decrease the \( \tan \delta \) value at the frequency where \( \tan \delta \) peak of soft matrix lies and that value drops very quickly with the increment of interphase thickness. 2) Although the outer interphase layer (IP1) has the same thickness as the one closer to hard domains (IP2), no \( \tan \delta \) peak occurs at the frequency where \( \tan \delta \) peak of IP1 lies. This indicates that the maximum shifting factor in the interphase domain determines the extent of \( \tan \delta \) shifting of the copolymer. However, IP1 is still indispensable not only from the physical meaning of decaying interphase, it also helps smooth the \( \tan \delta \) curve, unphysical double-peak might occur if we only apply a uniform interphase layer[111]. 3) Difference between IP-t1 and IP-t2 is much larger than that between IP-t4 and IP-t5. The reason is that, when interphase thickness increases, interphase layers of different hard domains can overlap, which leads to the fact that the volume fraction of hard domains does not increase proportionally to the incremental of interphase thickness. Detailed discussion on the overlapping interphase properties can be seen in Ref[159].

3. Effect of shifting factor distribution in the interphase layer

Since the interphase domain is the region where the mobility of soft matrix is gradually altered by hard domains, the property of interphase also gradually changes to that of the soft matrix when
it gets away from hard domains. The decaying pattern of interphase property is assumed to be in different forms, for example, exponential decay[102]. It’s not clear how changing this distribution will affect the final viscoelastic response. Here, with the same interphase geometry in Figure 47-(1), we apply two interphase property scenarios to this three-layer case: shifting factor to be 2.5, 1.5, 1 and 2, 1.5, 1. The maximum shifting factor for each case is given in Figure 47-(2) with dash-dotted and dotted curves respectively.

Figure 47 (1) Schematic of morphology adding three interphase layers. (2) effect of interphase property distribution on the response. Shifting factors are 2, 1.5, 1 for red curve and 2.5, 2, 1 for blue curve. The blue dash-dotted curve (Distribution1) specifies the IP layer with shifting factor to be 2.5 and the red dotted curve (Distribution2) gives that with shifting factor to be 2.

The property distribution across the same occupation of interphase areas makes a difference, as shown in the blue and red curves in Figure 47. Although both tan δ peak shift to left, the extents of shifting are different. The largest shifting factor in the interphase region determines the final shifting extent of the copolymer. In other words, how the property of the region closest to hard
domains are changed is critical when $\tan\delta$ peak shifting is studied. Furthermore, the variation of property distribution also changes the magnitude of $\tan\delta$ peak. Although all $\tan\delta$ peaks in soft matrix and interphase layers are assumed to be the same in all three cases in Figure 47, their locations are different. Therefore, the final $\tan\delta$ peak of the copolymer is a coupled result of the interphase’s spacial and property distribution.

4. Volume fraction of hard domains and volume fraction of interphase domains

There are various polyurea when $n$ is different in the repeating units $\langle C_4 H_8 O \rangle_n$ in the soft domains. Besides PU1000 discussed in this chapter, PU650 is another polyurea that’s commonly used. Applying the same procedure in Section 2 on the AFM phase image of PU650, a binarized geometry with a higher volume fraction but smaller size of hard domains is obtained (Figure 48-(2)). That allows us to incorporate the discussion on effect of volume fraction of hard domains, and further, the effect of volume fraction of interphase region, which is not brought by thicker interphase but by more hard domains.

![Figure 48 Schematic of morphologies with interphase layers](image)

(1) PU1000, volume fraction of hard domains = 15%
(2) PU650, volume fraction of hard domains = 27%

They both have two layers of interphase and thickness of each layer is the same.
As discussed in previous sections, elastic hard domains have no contribution to energy dissipation, which result in a further tan δ peak decrease with larger volume fraction of hard domains (blue and red curves in Figure 49, no interphase is added in these two cases). The difference of the tan δ peak decrease between PU1000 and P650 is smaller for the cases with interphase (cyan and magenta curves in Figure 49) than that without interphase. Although the overall tan δ curves decreases for a higher volume fraction of hard domains, the shifting pattern seems to remain, which indicates that the property distribution in the interphase area dominates the tan δ peak location of the copolymer instead of the copolymer’s composition. Quantitative analysis of volume fraction of both phases will be given in Section 5.4.

5. Modulus of hard domains

Adding interphase around hard domains mostly change the viscoelastic property of hard-soft copolymers in the transition region. The instantaneous storage modulus varies very little if no
change is made concerning the modulus of hard domains. Results in Figure 50-(1) also show that the long-term storage modulus is more dependent on the interphase property instead of hard domains. Lastly, variation in modulus of hard domains change the magnitude of $\tan \delta$ peak but barely influence its shifting behavior.

![Figure 50](image)

Figure 50 Effect of modulus of hard domains on the response of hard-soft copolymers. The legends for dashed curves in (1) are omitted for simplicity. Dashed curves are $E''$ as with their solid-curve counterparts in the same color. The dash-dotted curve is the $\tan \delta$ curve of the IP layer with maximum shifting factor, which is 2.

From the qualitative discussion above, we have a conceptual knowledge of how properties of interphase and hard domains affect the overall viscoelastic properties of the copolymers. However, a quantitative analysis is impossible with current description of interphase. For example, the feature, volume fraction of interphase, can be the result of both increasing the interphase thickness and increasing the volume fraction of hard domains. A clear mathematical description of interphase domain is needed, together with an algorithm to relate all the structural features with the aforementioned four response values.
5.4 Significance Ranking of Interphase Features Using Random Forest Algorithm

5.4.1 Vector Representation of Interphase

While how interphase thickness and property affect the overall performance of the copolymer is qualitatively presented in Section 5.3 with FEA simulation of the viscoelasticity, the contribution of each interphase feature on determining each response data is still unclear. For example, both interphase thickness and shifting factor distribution change the tanδ peak shifting, it’s hard to decouple the contribution of those two. To quantitatively present the feature significance, we first introduce a vector to represent the discrete interphase region, as in Figure 51-(1). The index (1-15) denotes the interphase location and the elements in the vector are the corresponding shifting factors at each specific location.

![Diagram](image-url)

(1)

<table>
<thead>
<tr>
<th>Case1</th>
<th>2 1 0 0 0 0 0 0 0 0 0 0 0 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case2</td>
<td>2 2 1 1 0 0 0 0 0 0 0 0 0 0</td>
</tr>
<tr>
<td>Case3</td>
<td>2 2 2 1 1 1 0 0 0 0 0 0 0 0</td>
</tr>
<tr>
<td>Case4</td>
<td>2 2 2 2 1 1 1 1 0 0 0 0 0 0</td>
</tr>
<tr>
<td>Case5</td>
<td>2 2 2 2 2 2 1 1 1 1 1 0 0 0 0</td>
</tr>
</tbody>
</table>

(2)
Figure 51 Schematic representation of the whole interphase area using a 15-element vector.

When the interphase layer is adjacent to hard domains (1st layer in Figure 51-(1)), the shifting factor is the largest. It means that the viscoelastic curves in that layer shift the most to the lower frequencies, resulting in transition region further moving to lowest frequencies. One thing that needs to mention is that, one element in the vector is not necessarily equivalent to one pixel, the thickness of each element is about 2 ~ 3 pixels based on the boundary shape of specific hard domains. One example is given in Figure 51-(2), of which the schematic of the morphologies is as in Figure 45. Shifting factors for Case 1 are 2 and 1, the length of nonzero elements in this vector represents the interphase thickness.

With such vectors, represent interphase features of interest with the statistical values of the vectors. Based on the qualitative analysis in Chapter 4, the structural features we choose are as in the following table,

Table 2 Statistical variables of a 15-element vector and their corresponding representation of physical meaning in an interphase.

<table>
<thead>
<tr>
<th>Statistical variables / overall structural properties</th>
<th>Corresponding physical meaning of variables</th>
<th>Feature labels for following discussion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of nonzero elements</td>
<td>Thickness of entire interphase</td>
<td>Th-IP</td>
</tr>
<tr>
<td>Mean value of the vector</td>
<td>Average level of interphase property</td>
<td>Mean-SFs</td>
</tr>
<tr>
<td>Standard deviation of the vector</td>
<td>Interphase property distribution</td>
<td>Sd-SFs</td>
</tr>
<tr>
<td>Volume fraction of interphase</td>
<td>Interphase occupation</td>
<td>VF-IP</td>
</tr>
<tr>
<td>Maximum value of the vector</td>
<td>Largest shifting value from matrix</td>
<td>Max-IP</td>
</tr>
<tr>
<td>Length of elements with max value</td>
<td>Thickness of the largest shifting layer</td>
<td>Th-IP(maxSF)</td>
</tr>
<tr>
<td>Volume fraction of layers with max value</td>
<td>Self-explained</td>
<td>VF-IP(maxSF)</td>
</tr>
<tr>
<td>A flag to specify w/o interphase</td>
<td>Self-explained</td>
<td>significantIP</td>
</tr>
<tr>
<td>Young’s modulus of hard domains</td>
<td>Self-explained</td>
<td>Modulus-H</td>
</tr>
<tr>
<td>Volume fraction of hard domains</td>
<td>Self-explained</td>
<td>VF-H</td>
</tr>
</tbody>
</table>
The four response variables are as chosen in Section 5.2, \( \tan \delta \) peak decrease, \( \tan \delta \) peak shifting, instantaneous storage modulus and long-term storage modulus. To identify the significance of ten features selected in Table 2 in determining the four response values, herein a machine learning based ranking approach, namely random forest regressor (RFR) [160] is utilized. RFR is an ensemble-based machine learning approach that fits a set of decision trees on various sub-samples of the dataset and uses averaging to improve the predictive accuracy and to prevent over-fitting. In each hierarchical level of sub-decision tree in the RFR model, features are used as splitting criterion to reduce the variance (aka. impurity) of data. For each feature, its contribution to the variance decrease is averaged across all the sub-decision trees, and the averaged variance decrease is utilized to rank the feature significance. In other words, features which lead to more variance decrease in RFR would be regarded as more important. Details of the algorithm can be found in Ref [160].

5.4.2 Brief Explanation of Decision Tree and Random Forest Algorithm

Before introducing the concept of decision tree, we first explain what impurity measurement of a dataset is. Given a data table that contains attributes and class of the attributes, we can measure homogeneity (or heterogeneity) of the table based on the classes. We say a table is pure or homogenous if it contains only a single class. If a data table contains several classes, then we say that the table is impure or heterogeneous. There are several indices to measure degree of impurity quantitatively. At each branch of a decision tree in this dissertation, it involves a round of impurity measurements.
A decision tree is a flowchart-like structure in which each internal node represents a "test" on an attribute (e.g. whether a coin flip comes up heads or tails), each branch represents the outcome of the test, and each leaf node represents a class label (decision taken after computing all attributes). The paths from root to leaf represent classification rules. For example, in a typical decision tree in Figure 52, if a splitting criterion with constraints of feature 1 is applied to the original dataset, we can measure the weighted impurity of two resulted sub-datasets. The weighting factors are the percentage of data from original dataset.

For each splitting, the algorithm goes through all possible criteria for each feature and selects the one with the least impurity. That feature is the splitting feature for this split. (e.g. feature 1 is the first splitting feature and feature 4 and feature 2 are two splitting features for the next level in Figure 52).
Random forest is an ensemble learning method for classification, regression and other tasks. It operates by constructing a multitude of decision trees at training time and outputting the class that is the mode of the classes (classification) or mean prediction (regression) of the individual trees [161]. Random decision forests correct for decision trees' habit of overfitting to their training set [162]. In this dissertation, bootstrap sampling is used to construct datasets from the original one. Bootstrap sampling means random sampling with replacements. Each sampling has the same number of data points as the original dataset.

Once the splitting process is done for each decision tree, we can use the random forest algorithm to do prediction. As in Figure 53, given a data point with known features (the data point is in the dataset which is specified with purple balls at each level), every decision tree will generate one prediction, final prediction is an average of all predictions in the random forest.
During the splitting and prediction process, it’s easy to see that random forest algorithm can be used to rank the importance of variables in a regression or classification problem in a natural way. In our case, the values of response are continuous values. Therefore, we choose the variance of the value of each response (variance of each dataset) as the impurity measurements. Then, we can compare the average variance decrease of each feature to determine the feature significance. The variance decrease of each feature measures the improvement it brings to the classification and thus it measures how important that feature is.

Here is how we calculate the average variance decrease of each feature. Take the case in Figure 54 as an example. The variance of the original data is \( V_0 \). After splitting with criterium concerning feature-1, the variance of two sub-datasets are \( V_{1-1} \) and \( V_{1-2} \). The variance decrease of feature-1 is \( \Delta V_1 = V_0 - V_1 = V_0 - (V_{1-1} \times 50\% + V_{1-2} \times 50\%) \). Another example is in the second level, after splitting with criterion concerning feature-2, the variance of two sub-datasets are \( V_{2-1} \) and \( V_{2-2} \). The variance decrease of feature-2 is \( \Delta V_2 = V_1 - (V_{2-1} \times 25\% + V_{2-2} \times 75\%) \). In the end, after the
splitting for each decision tree, there will be a variance decrease value for features occurred in that decision tree as splitting criterion. One thing to be noticed is that, it’s not necessarily true that all features will occur in one single decision tree. For example, feature-3 does not appear in Figure 54.

After the splitting procedure is complete in all decision trees, we have all features with their variance decrease values. The average variance decrease of each feature gives the final importance ranking of each feature in deciding this response dataset. In identifying the significant FE features in this work, the following prevalent setting of RFR parameters is utilized.

Table 3 Parameters for random forest used in this dissertation.

<table>
<thead>
<tr>
<th>Name of parameter</th>
<th>Value of parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of decision trees</td>
<td>10</td>
</tr>
<tr>
<td>Bootstrap sampling</td>
<td>True</td>
</tr>
<tr>
<td>Minimum number of samples for further splits</td>
<td>2</td>
</tr>
<tr>
<td>Number of features to check while looking for the best split</td>
<td>All features</td>
</tr>
</tbody>
</table>

5.4.3 Discussion of Ranking Results

After running the RFR with the ten features as inputs and four responses as outputs, quantitative importance of each feature in determining each response is given in Figure 55. Significant observations are:

(1) Volume fraction of hard domains is the most crucial factor when it comes to tanδ peak decrease because hard domains in our FEA model are pure elastic and cannot dissipate any energy during loading. Following that, volume fraction of total interphase area is also an important feature. Since the interphase property curves are shifting to the lower frequencies from soft matrix, the
$\tan \delta$ value decreases at the frequency where the $\tan \delta$ peak locates in soft matrix, which results in the peak decrease at the original frequency, but the $\tan \delta$ value will increase and may form a new peak when interphase occupation dominates at a lower frequency, like what happens in Figure 46.

It’s noticeable that the standard deviation of shifting factors is in the 3rd place while mean value of shifting factors is in the 4th place. To explain this, take three simple cases as an example:

$$
\begin{align*}
\text{IP}_1 &= [2.0,1.5,1.0], (\text{mean} = 1.5, \text{Sd} = 0.41) \\
\text{IP}_2 &= [2.5,1.5,0.5], (\text{mean} = 1.5, \text{Sd} = 0.82) \\
\text{IP}_3 &= [1.5,1.0,0.5], (\text{mean} = 1.0, \text{Sd} = 0.41)
\end{align*}
$$

The differences of $\tan \delta$ peak decrease between IP1 and IP2 is larger than that between IP1 and IP3 in Eqn. (27).
Figure 55 Significance ranking of ten structural and property features on $\tan \delta$ peak decrease, $\tan \delta$ peak shifting, instantaneous modulus and long-term modulus.

(2) Mean value of shifting factors in interphase domain dominates the $\tan \delta$ peak shift. This is as expected since adding IP layers with properties shifting to the lower frequency is the driving force for the $\tan \delta$ curve of copolymers’ response to shift left. The mean value of shifting factors indicates the average of the $\tan \delta$ peak location in interphase domains. When these interphase domains are included in the FEA model, it drives the shifting of $\tan \delta$ peak of the whole copolymer systems. In addition, the larger the volume fraction of interphase region (3rd place) is, the stronger this driving force is. Another two noteworthy features are volume fraction of IP layers with the
maximum shifting factor and the maximum value of that shifting factor. This is because these two factors define the upper limit that the $\tan \delta$ peak can shift. Imagine that the whole soft matrix is occupied with interphase layers with shifting factor to be $m$, the $\tan \delta$ curve of the whole copolymer will be shifted $m$ decades to the left.

(3) Modulus of hard domains determines the instantaneous storage modulus change at frequency range of glassy state. This is straightforward since instantaneous moduli of interphase layers are the same with that of soft matrix no matter what the shifting factors are. The increment of modulus in glassy state comes from the inclusion of hard domains. One thing to be noticed is that modulus of hard domains is much more important than its volume fraction.

(4) Volume fraction of hard domains dominates the long-term modulus change. Compared to the significance ranking to determine the instantaneous modulus, modulus of hard domains is less valued for long-term modulus. To increase the modulus of the copolymers in rubbery state, volume fraction of hard domains should be increased. Another important feature is the mean value of the shifting factors in the interphase domain. The long-term modulus increases when the interphase is stronger, and more interphase is involved.

5.5 Interphase Study via 3D voxelated FEA Model

2D pixelated FEA model is employed due to the need of a large amount of data for ranking analysis and the intrinsic large computational cost of 3D models. Despite that, 3D voxelated FEA model is implemented for the polyurea system to show that the predicted pattern of interphase impact on the overall performance from 2D cases is generalizable to 3D cases. A phase retrieval method [163] is conducted on the binarized phase image in Figure 41. Similar to what is done in
2D cases, interphase with different thickness and properties can be added. Figure 56 shows the schematic of morphologies adding interphases with one, two and three shifting factors.

Figure 56 Adding different interphase layers around hard domains in 3D models obtained from phase retrieval method.

Figure 57 $\tan \delta$ peak changes for 2D and 3D structures with the same interphase content, $\tan \delta$ of the soft matrix and two interphases are also given.

To compare results from 3D simulations with 2D ones, we choose a 2D structure and 3D structure with the same geometrical and property value for all features mentioned in Section 5.4. Figure 57 gives the $\tan \delta$ changes when no interphase is added to the 2D and 3D cases, as well as when the same interphase content is added to those two cases. The results clearly show that, values of $\tan \delta$ peak decrease from the 2D model is completely consistent with that from the 3D model.
After adding two layers of interphases, both tan δ peaks shifted to the lower frequencies. These results are important as it indicates the consistence between 2D and 3D analysis. Therefore, the 2D pixelated model saves computational cost.

5.6 Summary

The influence of the interphase dimension and content on the viscoelastic response of hard-soft copolymer systems is investigated through a 2D FEA model. The model takes the pixelated binary phase image from AFM as its geometry input while the material input comes from the DMA data at lower frequencies and MD estimations at higher frequencies. Gradient interphase is added around the hard domains and its properties are obtained by shifting the soft matrix property in the frequency domain. The shifting factor of each interphase layer depends on its distance from hard domains, corresponding to the change of altering effects on mobility of soft matrix brought by hard domains. With computational experiments on cases with different interphase thickness and property distributions, we present how these factors affect the viscoelastic response of copolymers. The simulation results indicate that relaxation characteristics of the hard-soft copolymers are greatly influenced by the interphase occupation and the shifting factors distributed across the interphase region.

To quantitatively present the interphase feature significance, the discrete interphase region is represented via a vector with shifting factors as its elements. Based on that, the statistical variables of the vector like mean and standard deviation which represent physical features of the interphase region, together with other factors like overall volume fraction of interphase, are selected as input features. Moreover, the response variables are tan δ peak decrease, tan δ peak shifting,
instantaneous storage modulus and long-term storage modulus. With ten input features and date of four response variables, a random forest algorithm is employed to rank the feature importance on determining each response. The results show that modulus of hard domains determines the instantaneous storage modulus change while the volume fraction of hard domains dominates the long-term modulus change. Besides volume fraction of hard domains, total interphase volume fraction and shifting factor distribution mainly affects $\tan \delta$ peak decreases while the mean and maximum value of shifting factors determine the $\tan \delta$ peak shifting.

Quantitative comparison between the experimental data and the model prediction is not possible at current stage due to the extreme difficulty in conducting experiments on polyurea to get complex local properties. Nevertheless, the impact of the interphase on the overall performance of the copolymer presented in this paper still provide significant observations to help understand the structure-property relation of this type of polymers.
Chapter 6  Summary and Concluding Statement

The work presented in this dissertation identifies a need for additional work in current research of thermoplastic polyurea and polyurethanes, the formulation of a research plan including computational work in both molecular scale and continuum scale, and an in-depth analysis to help understand the underlying mechanism in the relation between microscale structure and macroscale property of TPUs. This chapter gives a summary of contributions, a brief recap of the aforementioned limitations and a potential path for future research in this field.

6.1  Summary of Contributions

The work presented in this dissertation made several contributions to the study of hard-soft copolymers to address some of the current limitations in relating their microstructural features with their excellent mechanical properties. These contributions are summarized below:

1. Establishment of a CGMD model and mechanical response investigation of TPUs. A generic bead-spring coarse-grained MD model is employed to simulate the hard-soft copolymers. With a homogeneous bead-spring model as the base model, we introduce an energy factor to represent the interaction level between hard beads and replace soft beads with hard beads in specific patterns. Based on physical properties such as temperature dependent density and glass transition temperature from well-established and validated atomistic simulations, accurate input parameters for the CGMD models are derived and results from CGMD models can also be fitted and scaled from Lennard-Jones units to the real units. Critical information regarding the phase-separated microstructure and its evolution at various conditions are obtained from the CGMD model and they help us further understand the effect of composition and attraction of hard beads.
on the morphology of copolymers. To study the shear resistance of polyurea under pressure, factors such as applied pressure, shear strain rate, temperature, fraction of hard segments and interaction between hard beads need to be considered. After a parametric study conducted with various combinations of the above factors, we find that among all of the factors investigated, pressure is the most critical one because compression causes material densification, which increases stiffness. Moreover, when including pressure as a parameter in shear constitutive relations, both the initial shear moduli and shear strength are a piecewise linear function of pressure. In addition, the coupled effects of hard phase fraction and interaction between hard segments, together with temperature, also show considerable influence on the shear performance by contributing to the vitrification of hard domains.

2. Calculation of mechanical properties of soft and hard domains using CGMD model.

Because the soft matrix is in its rubbery state at room temperature and hard domains are more solid-like ($T_g$ of hard domains is around 100°C), elastic modulus of hard domains and viscoelastic property of soft matrix are calculated respectively using the CGMD model, together with the viscoelasticity of the hard-soft copolymers. First, a technique called stress autocorrelation is used to compute the dynamic shear modulus $G(t)$ to understand the stress relaxation of elastomers and how they mitigate damage in impact loading applications. Dynamic shear modulus $G(t)$ is then fitted with Prony series using a two-step optimization method. From $G(t)$ of copolymers with different compositions, we observe that soft matrix exhibits pure rubbery behavior, whereas the response becomes more solid-like with the addition of more hard segments. Furthermore, storage
and loss modulus curves in frequency domain are presented by transferring $G(t)$ into $G'(\omega)$ and $G''(\omega)$ with Prony series parameters. Second, local elastic constants of hard domains are computed by replacing global variables with local ones in a general stress-strain fluctuation algorithm. The definition of per-bead stress in LAMMPS is used and definition of local strain of a single bead is also introduced. Based on that, the local stress and local strain of a hard domain is the averaging effect of all hard beads in that domain. With that, the local elastic constants of hard domains are calculated with purely local stress and local strain tensors. Again, the coupled effect of hard phase fraction and interaction between hard segments dominates their elastic moduli. The obtained mechanical properties of each phase can be used as the inputs for continuum models for two-phase systems. Since the results are directly related to molecular features, they can provide new insights that will enable the tailoring of the microstructure of TPUs in order to optimize their performance in penetration and fragmentation resistance of metallic/polymer systems and to provide better understanding that reflects the influence of microstructure and composition on macroscopic properties.

3. Derivation/Definition of geometrical and material inputs for three phases (soft, hard and interphase) in FEA model and investigation of the interphase effect. To investigate the influence of the interphase dimension and content on the viscoelastic response of hard-soft copolymer systems through FEA models, both geometrical and material inputs are needed. We start from the AFM phase image and binarize the phase image into two phases after preprocessing. After adding gradient interphase layers around the hard domains, the binarized images with soft matrix, hard domains and interphase layers are the geometrical the geometry inputs required. On
the other hand, the material input of soft matrix comes from the DMA data at low frequencies and MD simulation results at high frequencies. Interphase properties are considered as similar with that of the soft matrix and are a simple shift to the low frequency range. The shifting factor depends on the distance from hard domains, corresponding to the change of altering effects on mobility of soft matrix brought by hard domains. After detailed analysis on cases with different interphase thickness and property distribution, we present how these factors affect the viscoelastic response of copolymers. Three frequency ranges are classified, among which interphase plays a crucial role in the mediate frequency range (transition region). The simulation results indicate that relaxation characteristics of the hard-soft copolymers are greatly influenced by the interphase occupation and the shifting factors distributed across the interphase area. Quantitative comparison between the experimental data and the model prediction is not possible at current stage due to the extreme difficulty in conducting experiments on polyurea to get such complex properties. Nevertheless, the impact of the interphase on the overall performance of the copolymer presented in this dissertation still provide significant observations to help understand the structure-property relation of this type of polymers.

4. Identification of interphase feature importance in impacting the copolymer’s mechanical response. To quantitatively present the significance of structural features on impacting the response, we first represent the whole interphase with a 15-element vector. The statistical variables of the vector like mean and standard deviation are set to represent physical features of the interphase quantitatively. Together with other factors like overall volume fraction of interphase, we extract ten structural and property features to describe the model with interphase
layers. In addition, the response data are chosen to be $\tan\delta$ peak decrease, $\tan\delta$ peak shifting, instantaneous storage modulus and long-term storage modulus. With ten structural features and four response datasets, a random forest algorithm is employed to rank the feature importance on determining each response. The results show that modulus of hard domains determine the instantaneous storage modulus change while the volume fraction of hard domains dominates the long-term modulus change. Volume fraction of hard domains is in the 1st place in impacting the $\tan\delta$ peak decreases, following it is the total interphase volume fraction and shifting factor distribution. The mean and maximum value of shifting factors in the interphase area determine the $\tan\delta$ peak shifting. Lastly, these predicted patterns of interphase impact on the overall performance from 2D cases is consistent with 3D cases but saves lots of computational cost.

6.2 Outlook into Future

The following research directions are recommended to extend the works presented in this dissertation:

1. **Extension of studies in molecular simulations.** First, molecular and coarse-grained modeling of shock wave mechanics in elastomeric polymers should be the next step with existed CGMD models or updated models. The shock wave attenuation and dispersion capability of polyurea is the reason for research in this area in the last three decades. In this dissertation, we relate the role of hard domains in the morphology and shear resistance under pressure, if a further step is taken, the mechanism responsible for the polyurea-enhanced shock wave mitigation can be found. The most frequently cited potential mechanisms for shock wave mitigation include: (a) shock wave-induced short and long-range ordering within the hard domains [164]; (b) shock wave-
induced crystallization/densification within the hard domains [164]; (c) breakage of the existing and the formation of new, and more numerous, hydrogen bonds within the hard domains [165, 166]; and (d) viscoelastic stress relaxation within the hard-domains and soft-matrix interfacial regions [167]. Second, models that can reach phase-separated state while considering moderate crosslinking are needed. 500 chains with 100 beads in each chain are included in our simulation box in this dissertation, which is large enough to mimic phase separation and to calculate most mechanical properties of interest. Due to computational limitations the simulations are limited to studying linear chains with above simulation box size. However, the experimental polyurea chains are much larger and also likely involve some crosslinking across chains. Existed studies to carry out the crosslinking reactions (static crosslink process) [168] and other computational studies [169, 170] involving crosslinking were performed on relatively small model systems (less than 10000 atoms), which is not large enough to show phase separation and to study mechanical properties of interests. Therefore, developing a model that can be large enough and fast enough to show phase separation while considering crosslinking is one direction.

2. **Experimental efforts on detailed information of both phases and mechanical property distribution in polyurea systems.** The molecular structure of polyurea has long been studied and it has been theoretically clear that hard segments are typically microphase segregated into the so-called “hard domains” because of strong hydrogen bonding between urea linkages of the neighboring chains (or the neighboring portions of the same chain). Tapping-mode AFM phase images in Figure 16 [140] also show the phase separation. However, high-quality phase images are barely reported since then. In addition, experimental efforts on detailed information of
mechanical property distribution is seldom reported due to the complex composition of polyurea. With more advanced experimental facilities and techniques, information obtained in this field will help validate computational results and further improve simulation models.

3. **Further simulation study in continuum scale.** First, development of constitutive models for polyurea films is always a crucial topic because the mechanical principles critical in realizing the versatility of this elastomeric segmented copolymer are incompletely understood at present. With the help of the three-phase model in this dissertation, a microstructure-based constitutive model of polyurea with varied fractions of hard and soft contents can be obtained. Loading with high strain rate and high pressure can be applied on both the three-phase polyurea structure and the homogenized model. Then, the constitutive models can be tuned by comparison between results from those two structures. The constitutive models can be linear viscoelastic, visco-elastic-plastic, or viscoelastic-viscoplastic, which depends on research goals. Second, it can provide valuable information to study the wave propagation behavior if one carries out impact loading test on bulk polyurea with more than two phases (soft matrix, hard domains and different interphase layouts). The macroscopic response of the polyurea and the role of hard domains under wave propagation can be investigated in a more realistic scale. Third, when carrying out experimental or computational assessments of the blast-mitigation efficiency of various elastomer-coating-based structures, real-life structures like building walls and vehicle body panels are typically replaced with plate-like surrogate test-structures. Therefore, polyurea film and steel substrate can be a simplified model to tune the constitutive model of polyurea under impact loading. In this simplified film/substrate model, various factors may influence the response. For example,
microstructural factors that will change film properties like composition and contraction inside the copolymer, which needs the correlation with detailed simulation of polyurea in this dissertation. On the other hand, there are also macrostructural features like film position, film thickness, interphase between film and substrate (e.g. perfect bonding or allow interface to be sliding or detached).
Chapter 7  References


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